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# **A Study of the Preparation and Reactions of Titanium (IV) Carboxylates**

by  
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A thesis submitted as part requirement for the degree of Doctor of  
Philosophy of the University of Warwick.

The work herein reported was carried out between October 1984  
and September 1987 in the Department of Chemistry.



September 1988

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## ***DECLARATION***

Part of the work on the hydrolysis reactions of  $\text{TiCl}_3(\text{RCO}_2)$  complexes reported upon in this thesis was previously published in:

N.W. Alcock, P.N. Bartlett, D. Gordon, T.F. Illson and M.G.H. Wallbridge, *J. Chem.Soc.,Chem.Comm.*, 1986, 614

## SUMMARY

This thesis describes preparative methods for a number of titanium (IV) trischloromonocarboxylates,  $\text{TiCl}_3(\text{RCO}_2)$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $(\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{C}$ ,  $(\text{CH}_3)_2\text{CH}$ ,  $(\text{CH}_3)_3\text{C}$ ,  $\text{C}_9\text{H}_6\text{N}$ , *o* -  $\text{CH}_3\text{C}_6\text{H}_4$ , *p* -  $\text{CH}_3\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_2(\text{CH}_3)_3$ ,  $\text{C}_6\text{H}_5\text{CH}=\text{CH}$  and  $\text{CH}_3\text{CH}=\text{CH}$ ). The reactions of some of these carboxylates with oxygen and nitrogen donor ligands are also described.

An X-ray crystallographic study of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CO}_2]$  showed that the complex exists as trimeric molecules in the solid state. Cryoscopic molecular weight and  $^1\text{H}$  NMR experiments indicated that the complex dissociates into dimers in solution.

The structure of  $\text{Ti}_2\text{Cl}_7(\text{CH}_3\text{CH}=\text{CHCO}_2)(\text{CH}_3\text{CH}=\text{CHCO}_2\text{H})$  is reported. The complex has a triply bridged structure with two bridging chlorine atoms and a carboxylate bridge linking the titanium centres.

Hydrolysis reactions of  $\text{TiCl}_3(\text{RCO}_2)$  species are described and an unusual  $^{17}\text{O}$  exchange effect in esters was observed. A mechanism based upon the  $\text{A}_{\text{AC}}2$  ester hydrolysis mechanism is proposed for this effect. Cyclic Voltammetry experiments on  $[\text{TiCl}_2(\text{C}_6\text{H}_5\text{CO}_2)\text{EtOAc}]_2\text{O}$  indicate that both Ti (IV) centres are reduced to Ti(III) and that the reduction product reacts with a component of the solution to regenerate the starting material.

Some titanium-magnesium bimetallic complexes were prepared and characterised.



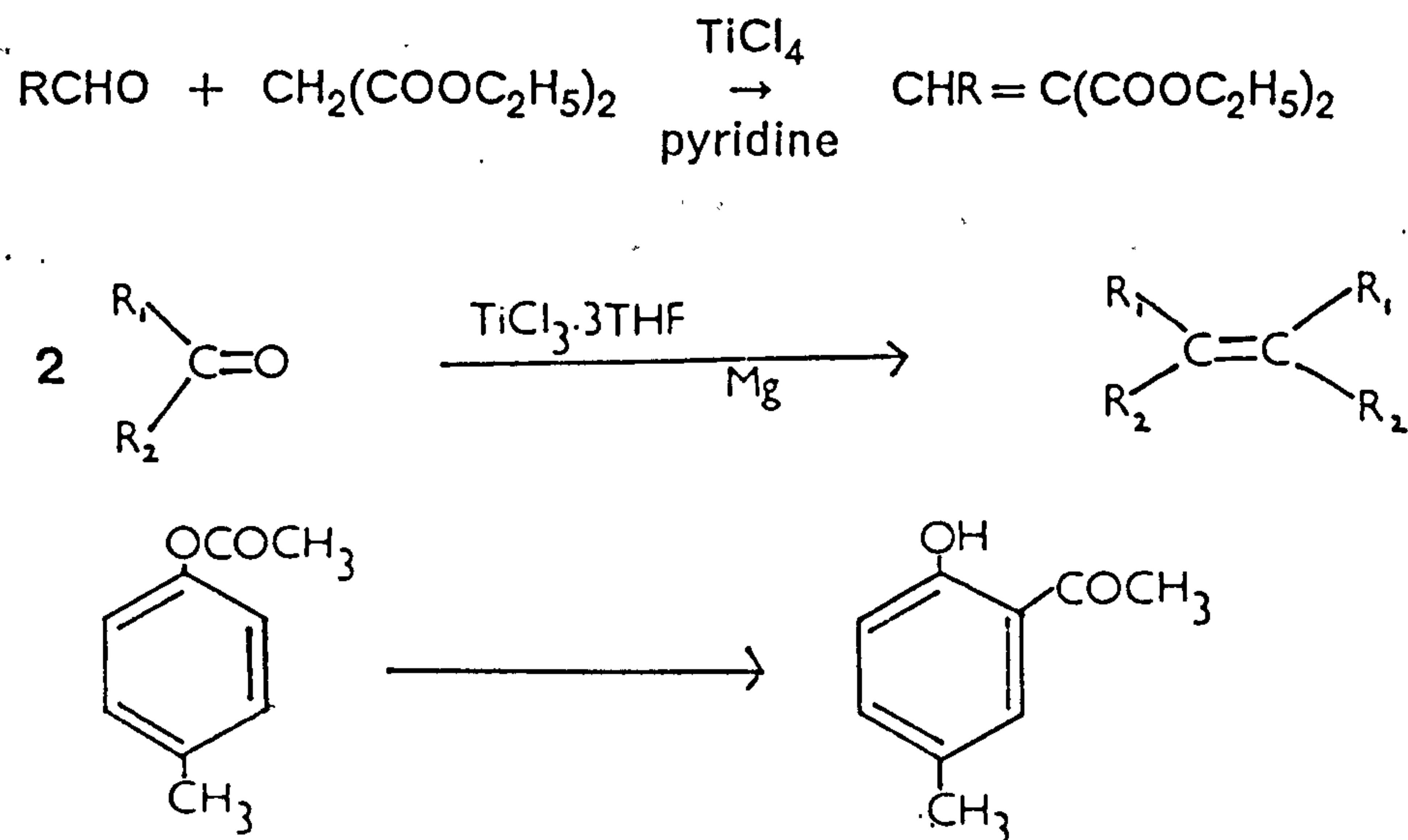
## ABBREVIATIONS

A	amps
Ac	acetyl $\text{CH}_3\text{C}=\text{O}$
acac	acetylacetonate $\text{C}_5\text{H}_7\text{O}_2$
B	bidentate ligand
b	broad
bipy	2,2' - bipyridyl
Cp	cyclopentadienyl ligand $\text{C}_5\text{H}_5^-$
d	doublet
DIAE	diisopentyl ether (diisoamyl ether)
$E_{p,c}$	cathodic peak potential
$E_{1/2}$	half wave potential
Et	ethyl $\text{C}_2\text{H}_5$
EtOAc	ethy acetate $\text{CH}_3\text{COOC}_2\text{H}_5$
ipa	anodic peak current
ipc	cathodic peak current
i.r.	infra-red
L	monodentate ligand
m	in infra-red = medium
m	in NMR = multiplet
Me	methyl $\text{CH}_3$
NMR	nuclear magnetic resonance
OEP	octaethylporphinato
Ph	phenyl $\text{C}_6\text{H}_5$
phen	1,10-phenanthroline
p.p.m.	parts per million
py	pyridine $\text{C}_5\text{H}_5\text{N}$
pyH	pyridinium ion $\text{C}_5\text{H}_6\text{N}^+$
q	quartet
R	alkyl or aryl group
s	in NMR = singlet
s	in infra-red = strong
sh	shoulder
t	triplet
THF	tetrahydrofuran $\text{C}_4\text{H}_8\text{O}$
TMS	tetramethylsilane $(\text{CH}_3)_4\text{Si}$
V	volts
w	weak

## CHAPTER 1.

## INTRODUCTION

Considerable interest in titanium chemistry has been generated by the ability of some titanium compounds to catalyse or accelerate the reactions of organic molecules(1). Some examples are illustrated below:

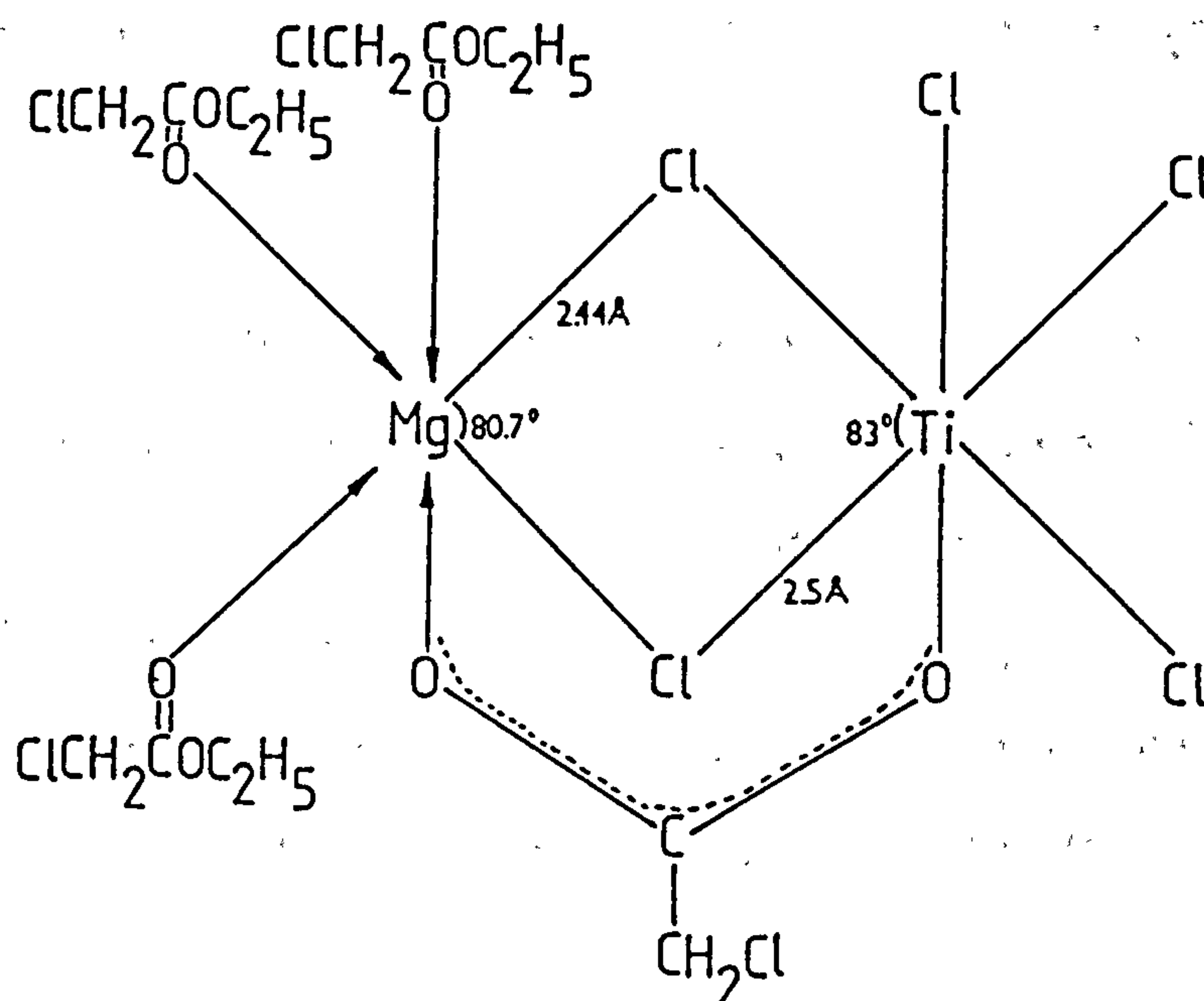


There are many examples of such reactions; however the most significant industrially is the polymerisation of olefins by titanium based Ziegler-Natta catalysts(2). In 1980 over a million tons of polypropylene was made using Ziegler catalysts in Western Europe alone(3).

A Ziegler-Natta polymerisation catalyst consists of a titanium halide in combination with an aluminium alkyl. A more recent modification combines the titanium component with an aromatic ester, the catalyst is then mixed with an inert support. Ziegler-Natta catalysts are discussed in more detail later.

There is some evidence that when titanium tetrachloride and esters are used in the catalyst then titanium carboxylates are formed(3). The compound  $\text{TiMgCl}_5 (\text{O}_2\text{CCH}_2\text{Cl}) (\text{ClCH}_2\text{COOC}_2\text{H}_5)_3$  formed by the reaction of titanium tetrachloride, magnesium chloride and ethyl

chloroacetate contains a carboxylate group formed by cleavage of the ester.<sup>(12)</sup> Its structure is shown below. It is possible that titanium carboxylates are present in supported Ziegler-Natta catalysts.



A literature search revealed very little reliable information on the chemistry, properties or structures of  $\text{TiCl}_x (\text{RCO}_2)_{4-x}$  ( $\text{R} = \text{alkyl, aryl; } x = 1, 2, 3$ ) species so it was decided, in consultation with ICI plc, to study the  $\text{TiCl}_3 (\text{RCO}_2)$  species.

This thesis reports preparative methods and some chemistry for a range of titanium (IV) tris(chloro)monocarboxylates. Also reported is the first crystal and molecular structure of a  $\text{TiCl}_3 (\text{RCO}_2)$  compound.

Some work has also been carried out, in this study, on titanium-magnesium bimetallic species containing carboxylate groups.

Hydrolysis reactions of the  $\text{TiCl}_3 (\text{RCO}_2)$  complexes have been examined, and an unusual  $^{17}\text{O}$  exchange effect in esters has been observed.

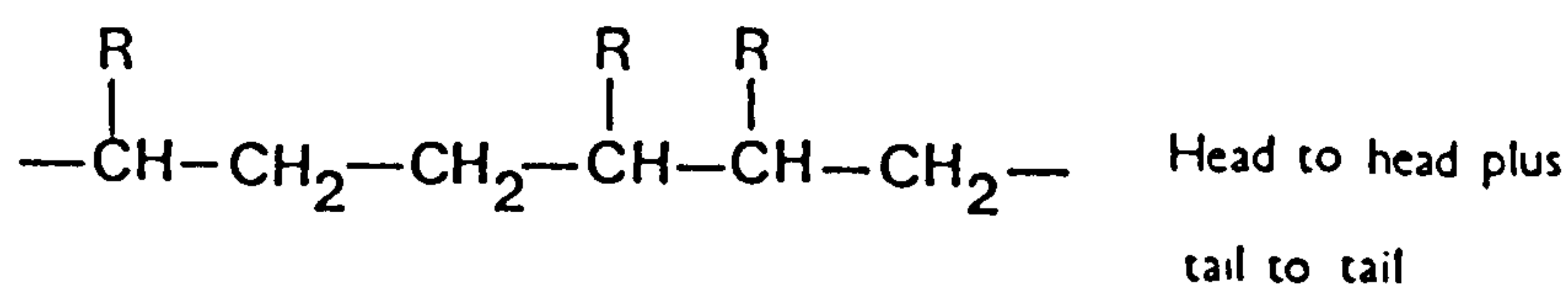
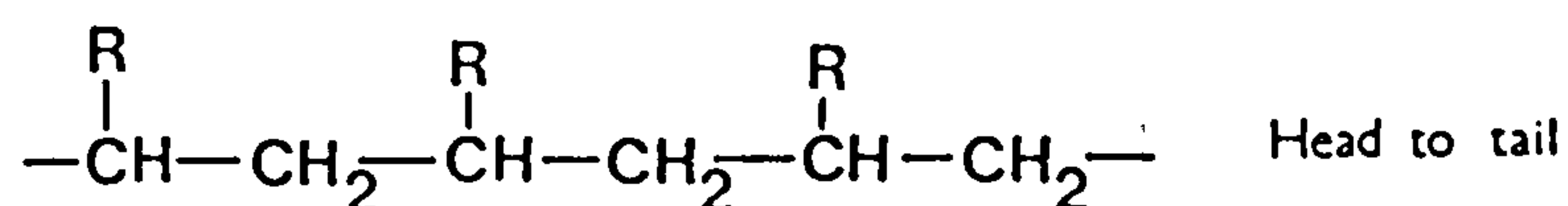
The following introductory chapter contains background information and is of necessity selective. In particular only titanium chemistry relevant to the thesis is included in the general sections.

## ZIEGLER-NATTA TYPE OLEFIN POLYMERISATION CATALYSTS

The discovery by Ziegler<sup>(4)</sup> that a catalyst comprising a transition metal compound and an organometallic derivative of a group I, II or III element will polymerise ethene at room temperature and atmospheric pressure revolutionised the world's bulk plastics industry. Previous catalysts required high pressures and high temperatures to produce polyolefins so Ziegler's catalytic system was superior in these respects.

Many variations on the original catalysts have since been patented for the production of polyethene, but it proved more difficult to discover a catalyst which would polymerise propylene into a useful form of polypropylene.

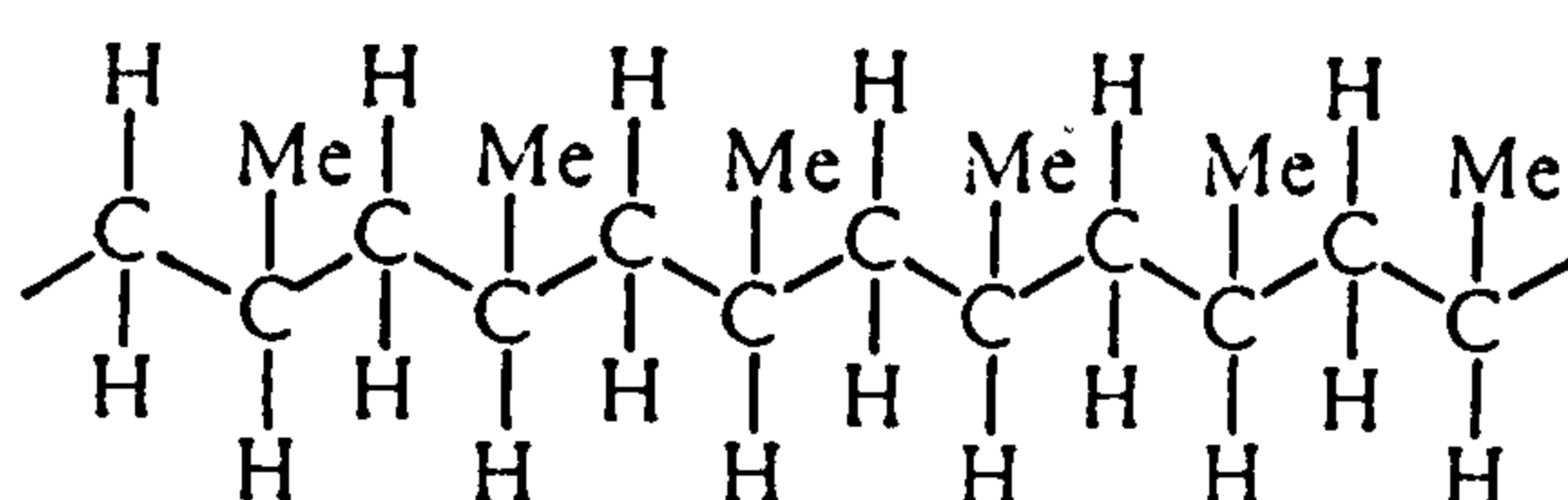
A variety of isomeric forms of polypropylene can be made; head to tail and head to head plus tail to tail units can be produced.



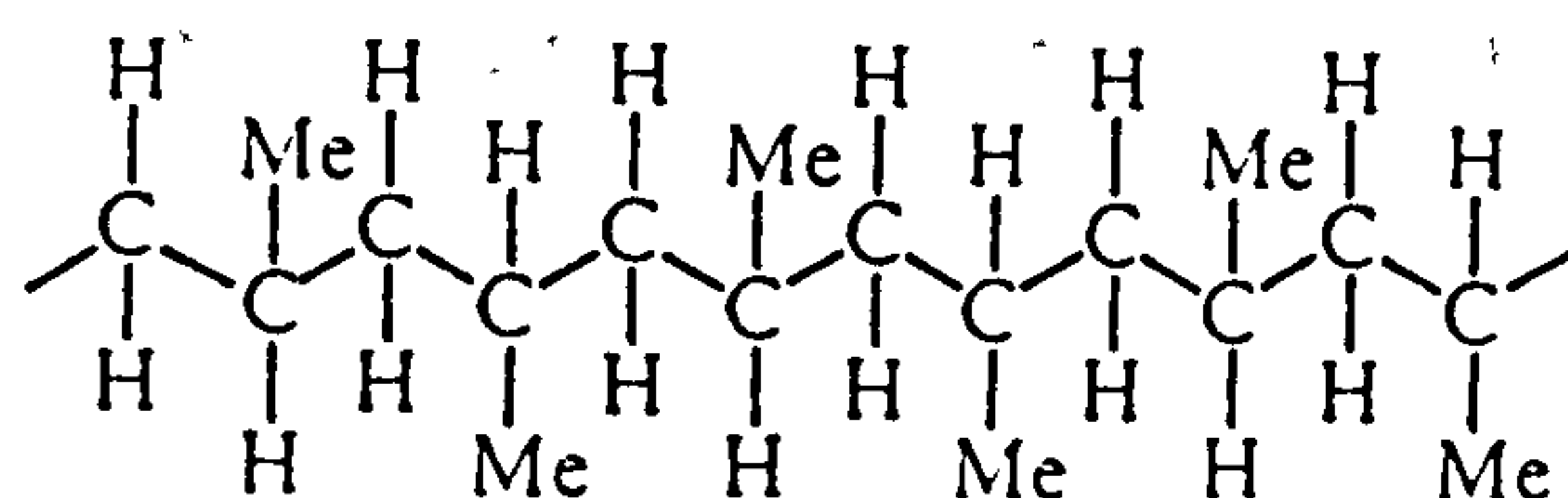
R=Me



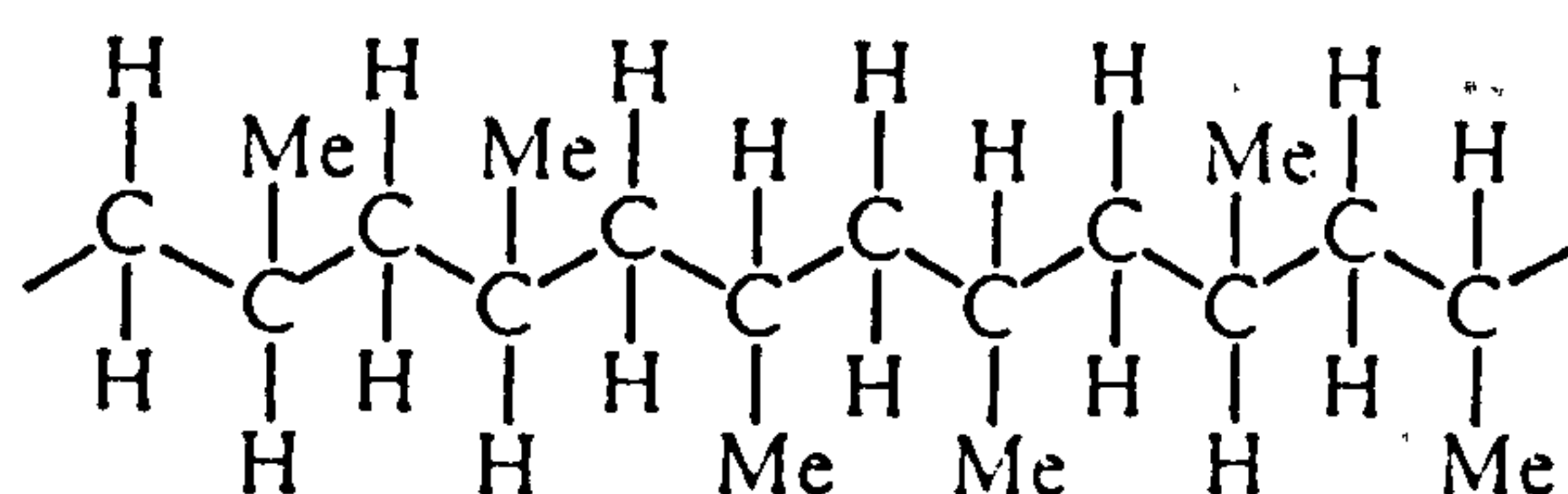
Head to tail units are most common but can exist in a number of different forms. If the polymer backbone is laid out as a zigzag line then the methyl groups may be either above or below the backbone. Isotactic polypropylene has all groups on one side of the backbone, syndiotactic polypropylene has the groups alternating between above and below the backbone and atactic polymer has random arrangement of the methyl groups.



Isotactic



Syndiotactic



Atactic

Isotactic and syndiotactic polymers have desirable properties from the industrial viewpoint so a successful catalyst must maximise the proportion of these forms in the polymer produced.

Most propylene polymerisation catalysts are based upon  $\text{TiCl}_3$ . It has been found that the  $\alpha$  form of  $\text{TiCl}_3$  gives increased yields of



stereoregular polymer compared with the  $\beta$ ,  $\gamma$  or  $\delta$  forms(5).The titanium trichloride is activated using an alkyl aluminium compound such as  $\text{AlEt}_3$ , or a diethylaluminium halide; the activator can also affect the activity and stereospecificity of the catalyst.

Attempts have been made to improve the basic  $\text{TiCl}_3$ /alkyl aluminium catalyst. One method of doing this is addition of a Lewis base. The Lewis base may either be added along with the activator or incorporated into the catalyst itself. A wide range of Lewis bases have been used including amines, phosphines, phosphites, ethers, esters and sulphur or boron compounds(6).

The Lewis base acts in a complex manner since it is capable of interaction with both the titanium trichloride and the aluminium alkyl activator. The base may remove catalytic poisons as complexes and assist in the fragmentation of the catalyst increasing the number of active sites. It can also increase the stereoregularity of the polymer produced.

The base is incorporated into the catalyst by milling a mixture of the base and  $\text{TiCl}_3$ . A successful catalyst is only produced when the temperatures and times used in each step of the milling process are correct. Some catalysts of this type are commercially important, their activity being so high that only chlorine residues need to be removed from the highly stereospecific polypropylene formed. Some examples of these catalysts are shown in Table 1.1.

Another type of catalyst is that patented by Solway and Cie(7).This catalyst consists of alkyl reduced titanium tetrachloride treated with diisopentyl ether and then treated with titanium tetrachloride. The catalyst uses a

diethyl aluminium chloride activator in polymerisations. It is a very active catalyst giving polymer yields of 715g polymer (mmol Ti)-1h-1. Its composition is  $\text{TiCl}_3 (\text{AlEt}_n\text{Cl}_{3-n})_{0.032}(\text{DIAE})_{0.061}$ . Its activity is due to the high surface area of the spherical microparticles of which the catalyst is composed. Good stereospecificity is also achieved.

## SUPPORTED CATALYSTS

As only a small proportion of titanium atoms form active sites in the catalyst much of the bulk titanium trichloride may be replaced by an inert support without affecting polymer properties.

The components of a successful supported catalyst are very limited. They consist of magnesium chloride, an aromatic ester, and titanium tetrachloride. The catalyst is used together with a triethylaluminium activator and another aromatic ester.

The range of support materials usable in a successful catalyst is also very limited. Magnesium chloride is the most effective followed by manganese dichloride. It appears magnesium chloride is the best material because its crystal structure is similar to that of  $\alpha$  or  $\gamma$   $\text{TiCl}_3$ , the material which it replaces. The  $\text{Ti}^{4+}$  and  $\text{Mg}^{2+}$  ions also have similar ionic radii thus making the two parts of the catalyst compatible.

To achieve the required polymer stereoregularity it is important to mill the  $\text{MgCl}_2$  with the aromatic ester and then treat with  $\text{TiCl}_4$  rather than milling  $\text{MgCl}_2$  with the  $\text{TiCl}_4$  ester complex(8).

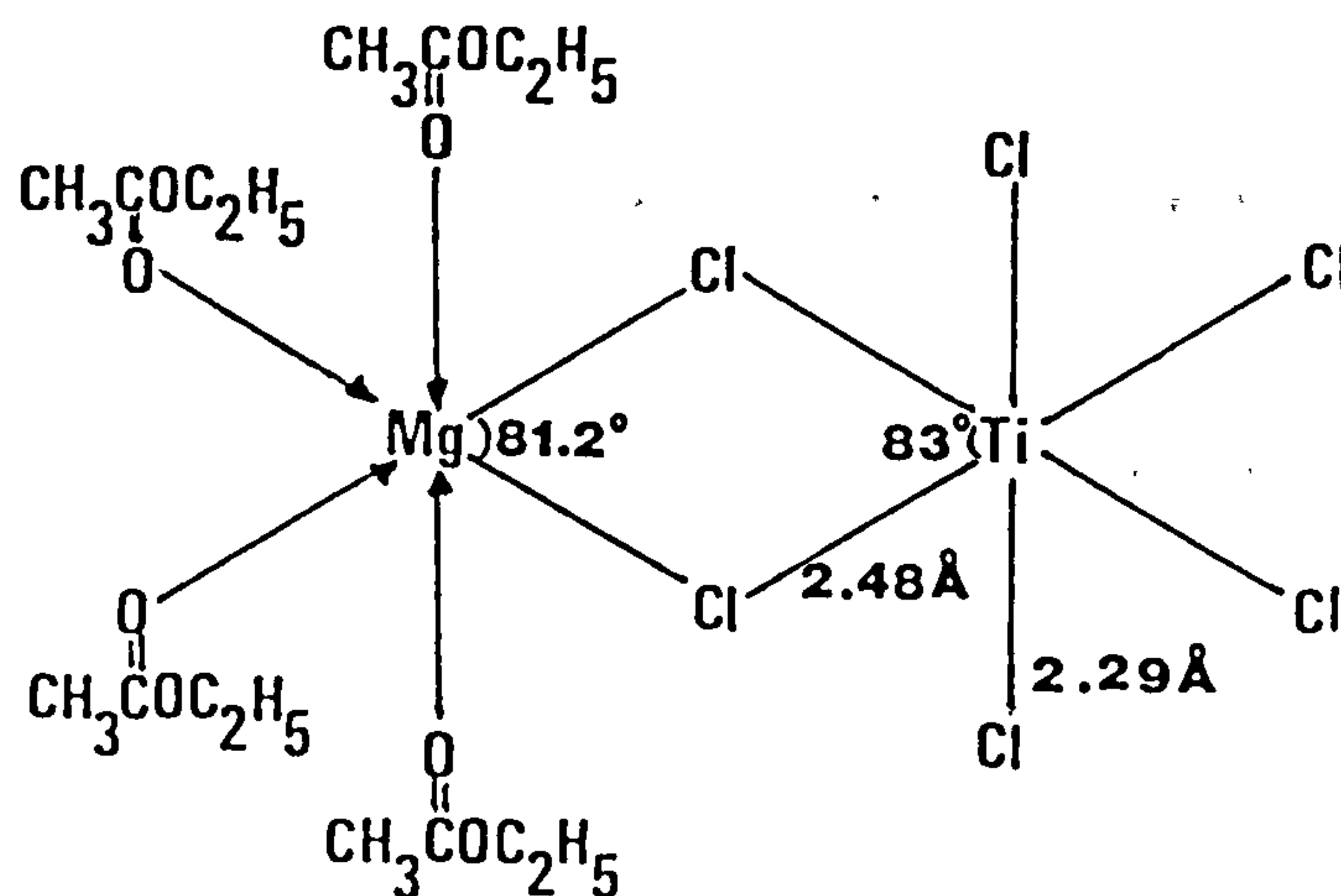
Table 1.1 : Catalyst Activities

Catalyst	Chem. Abstr. Ref.	Yield (gmmol-1h-1atm-1)
AlCl <sub>3</sub> . 3TiCl <sub>3</sub> milled with (EtO) <sub>4</sub> Si and methyl Methacrylate.	<u>84</u> ; 31,747	6
TiCl <sub>3</sub> treated with thioether used with n-propyl or n-hexyl-aluminium alkyl.	<u>91</u> ; 175, 965	3260a
TiCl <sub>3</sub> . Et <sub>2</sub> AlCl treated with TiCl <sub>3</sub> and (EtO) <sub>3</sub> P	<u>91</u> ; 21, 725	3.5
AlCl <sub>3</sub> . TiCl <sub>3</sub> milled with an ether e.g. <sup>n</sup> Bu <sub>2</sub> O, diisopentyl ether or MeOPh.	<u>89</u> ; 90,478	13

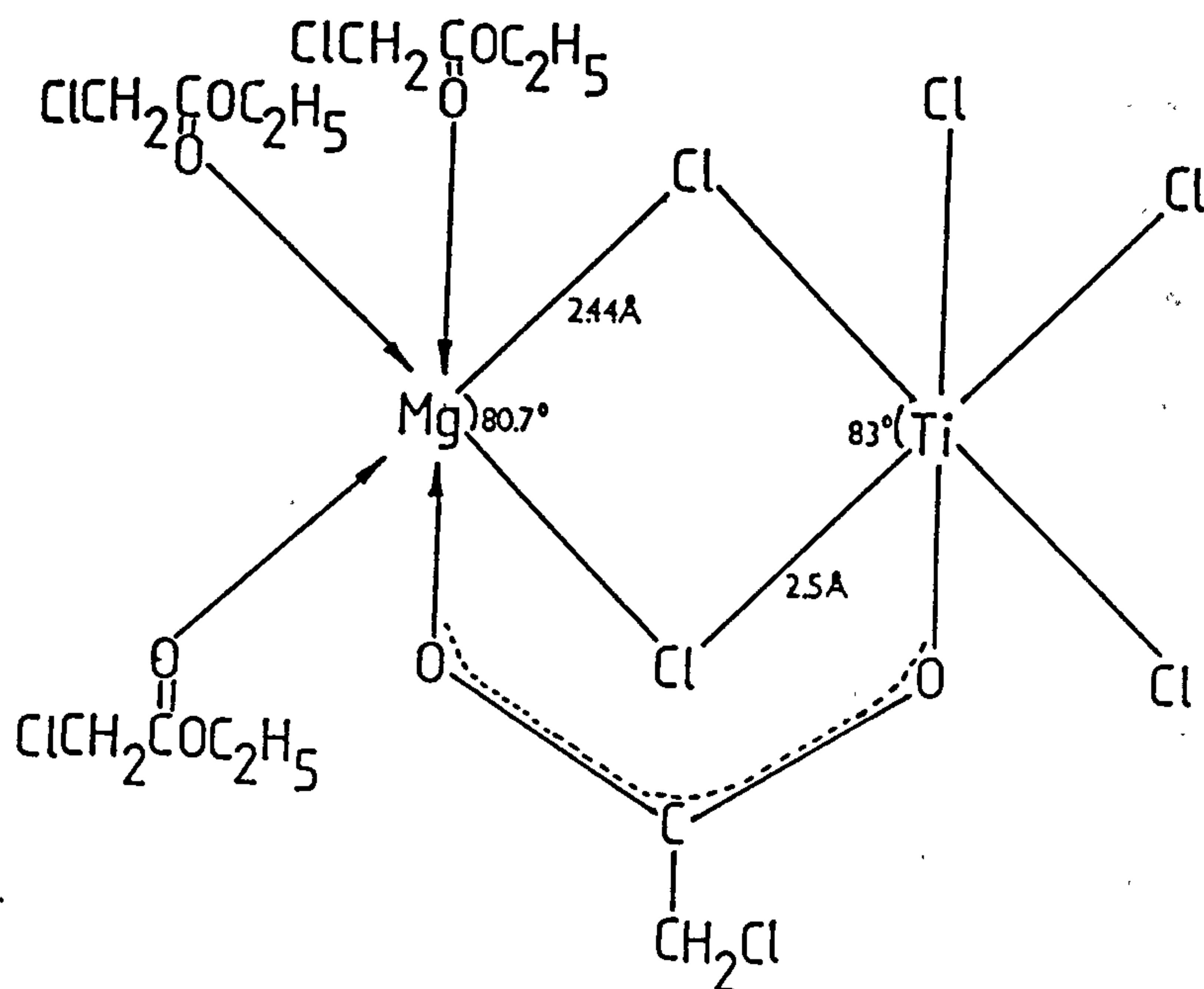
agmmol-1

The only Lewis bases which can be used to prepare successful supported catalysts are aromatic esters. These are the only Lewis bases which will produce the high stereospecificity required in the polymer. Best results appear to be obtained using the methyl and ethyl esters of benzoic, toluic or anisic acids. Ciardelli has shown that if the Lewis base reacted with the  $\text{MgCl}_2$  is optically active the polymer produced will also be optically active(9).

Little evidence exists as to the nature of the molecular species in this type of catalyst. Infra-red spectra of catalysts in which  $\text{MgCl}_2$  is milled with titanium ester complexes suggest the ester is bound to the magnesium(10). The molecular species present may be similar to the  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 4 \text{EtOAc}$  complex whose structure has been determined by Bart et al(11).



Another possible model is the triply bridged species  $\text{TiMgCl}_5 (\text{O}_2\text{CCH}_2\text{Cl}) (\text{CH}_2\text{ClCOOC}_2\text{H}_5)_3$  prepared and structurally characterised by Bassi et al(12). This complex contains a  $\text{CH}_2\text{ClCO}_2^-$  bridge from an ethylchloroacetate molecule which has lost an ethyl group becoming bonded to both the titanium and magnesium atoms.



The structure of  $\text{TiMgCl}_5(\text{ClCH}_2\text{CO}_2)(\text{ClCH}_2\text{COOC}_2\text{H}_5)_3$ .

It is therefore possible that such ester cleavage may occur in the supported catalysts producing carboxylate bridges.

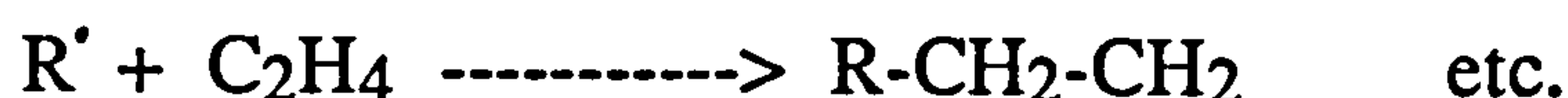
## THE MECHANISM OF ZIEGLER-NATTA CATALYSIS

The mechanism of Ziegler-Natta catalysis has still not been completely established. There have been four types of mechanism proposed to explain the polymerisation of olefins by Ziegler-Natta catalysts. These are:

- (i) A radical mechanism.
- (ii) An anionic mechanism.
- (iii) Mechanisms involving growth at the activator alkyl.
- (iv) Mechanisms involving propagation at a transition metal-carbon bond.



The earliest suggestion was the radical mechanism; various initiators were proposed, the transition metal centre by Friedlander and Oita (13), the aluminium centre by Duck (14) or an alkyl radical by Nenitzescu (15). Some monomers, for instance vinyl chloride, do polymerise by a radical mechanism in the presence of Ziegler-Natta catalysts but Ziegler-Natta polymerisation of ethene gives a different type of polythene to that produced by high pressure radical processes.



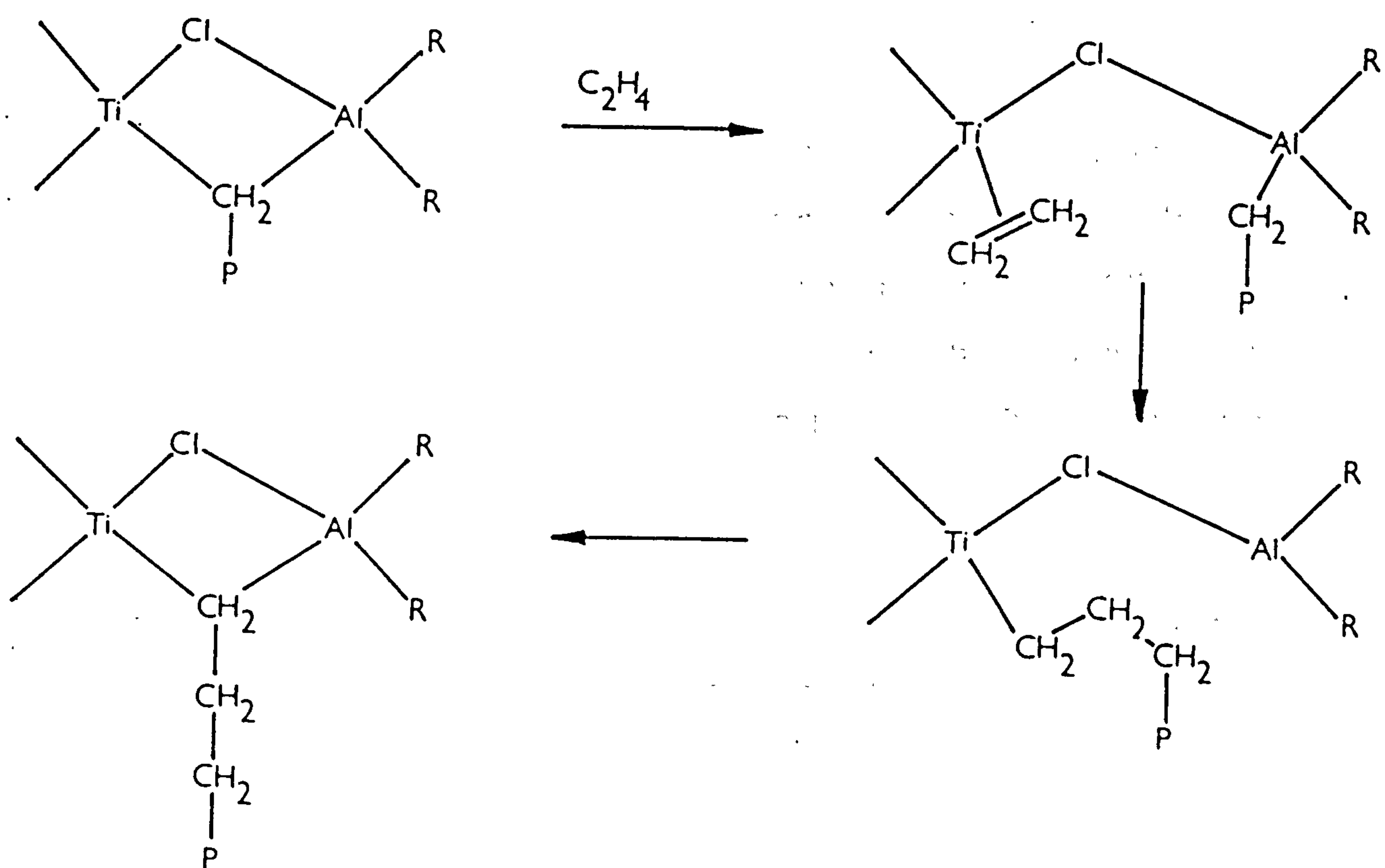
The Nenitzescu radical mechanism.

The anionic mechanism was proposed by Gilchrist (16). In this mechanism the polymer chain ends in an anionic carbon which is not bound to a metal. Initiation occurs by transfer of an alkyl anion from the metal alkyl to an absorbed alkene.

The most likely mechanisms are those in which growth occurs at a metal-alkyl bond. This could be an alkyl bond to the transition metal, to the activator or an alkyl bridging the transition metal and activator centres. Some evidence exists which supports the idea of the propagation centre being a metal alkyl bond. This evidence was obtained by using  $^{14}C$  labelled aluminium alkyl (17) or by introducing  $2H$  or  $3H$  as a chain transfer agent (18).



Mechanisms proposing propagation at the activator alkyl were proposed by Natta (19) and by Patat and Sinn. (20) These both involve the growing polymer chain acting as a bridging group between aluminium and titanium. In Natta's mechanism an alkene forms a  $\Pi$  -bond with titanium breaking the bridge, the polymer chain then moves onto the alkene which has formed a  $\sigma$  bond with the titanium due to polarisation. Then the polymer bridge reforms.



The Natta mechanism.

The most generally accepted mechanism for olefin polymerisation by Ziegler-Natta catalysts is that proposed by Cossee and Arlman. (21) In this mechanism polymerisation occurs at surface titanium atoms with a vacant coordination site. The activator replaces one chlorine on the titanium by

an alkyl. Then the alkene complexes at the vacant site and via a four membered cyclic intermediate the alkyl group is transferred to the bound alkene which is now  $\sigma$  bonded to the titanium. The alkyl ligand and the vacant site then exchange positions and further insertion occurs. This mechanism is shown in Figure 1.1.

A similar mechanism is that suggested by Rodriguez and Van Looy(22). The chief difference being that the polymer chain is considered to bridge between the transition metal and activator.

Green and Rooney (23) have proposed a mechanism involving a metal hydride carbene intermediate formed by a 1,2 hydrogen shift from the growing polymer chain to the transition metal centre. Alkene then coordinates to the transition metal and interacts with the carbene to form a metallocyclobutane. The hydride then returns to the tertiary carbon atom and the process continues.

Grubbs and coworkers (24) have shown using isotope stereochemistry experiments that the Green mechanism does not apply to Ziegler-Natta polymerisation.

## STEREOSPECIFICITY IN ZIEGLER-NATTA POLYMERISATION

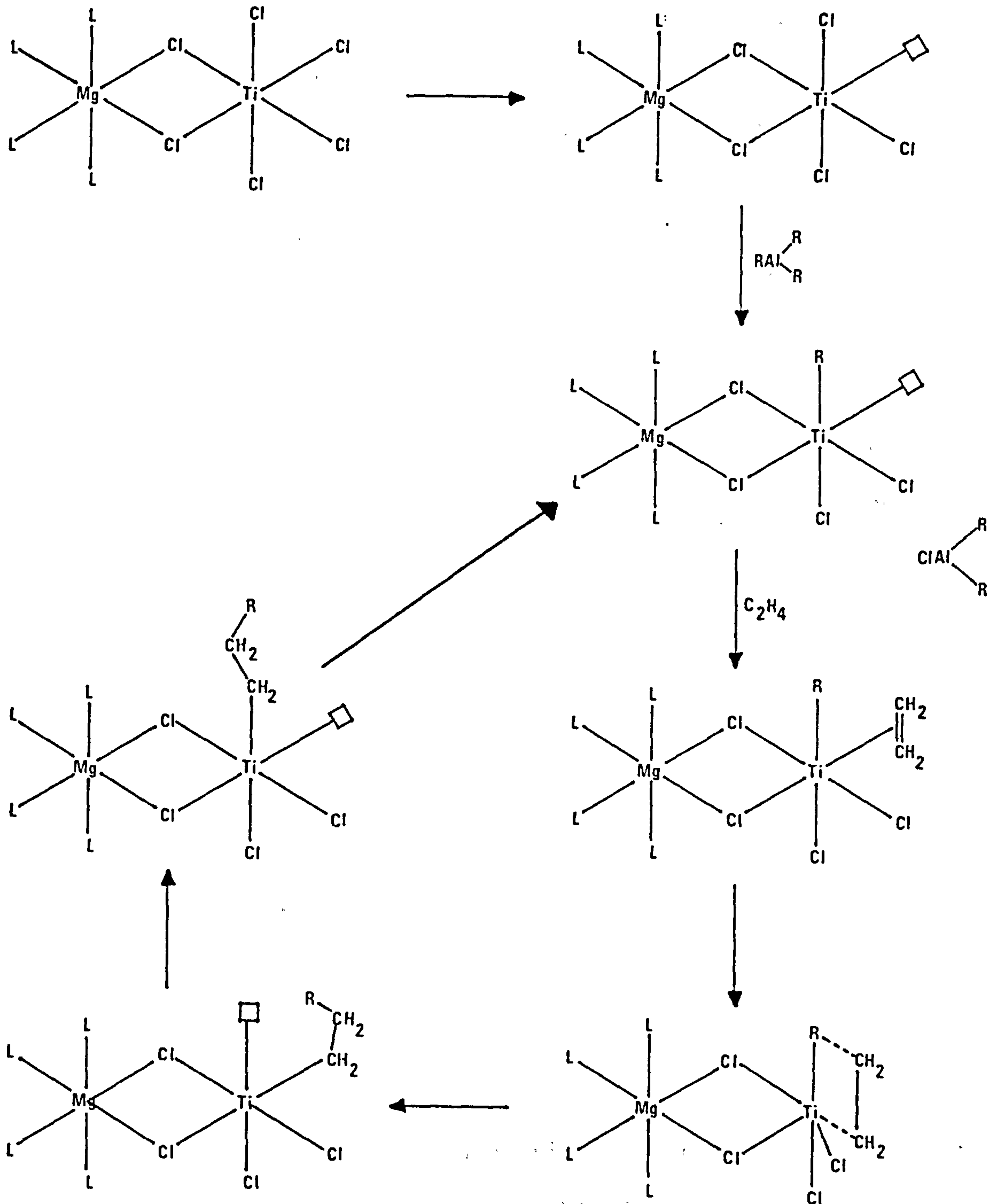
Crystalline isotactic polymer is the desired product for commercial Ziegler-Natta polymerisation processes. The stereospecificity is controlled by steric interactions. Zambelli and coworkers have shown by  $^{13}\text{C}$  NMR(25) that isotacticity is caused by the asymmetry of the transition

metal centre, and that syndiotactic stereocontrol is due to the influence of the last monomer unit in the polymer chain.

Orientation of the inserting monomer is also of importance. Cossee(26) suggested that isotactic polymerisation occurs due to monomer molecules only being able to fit into the vacant site postulated in his mechanism(21) with the  $\text{CH}_2$  group pointing into the  $\text{TiCl}_3$  lattice and a  $\text{CH}_3$  group pointing out of the surface.

An  $\alpha$  - alkene may add to the polymer chain in two different ways. It may bind the unsubstituted carbon atom to the active centre (primary addition) or it may bind the substituted carbon atom to the active centre (secondary addition). It has been shown that isotactic polymerisation proceeds via primary addition (27) and syndiotactic polymerisation proceeds via secondary addition.(28)

Figure 1.1 : The Cossee and Arlman mechanism.



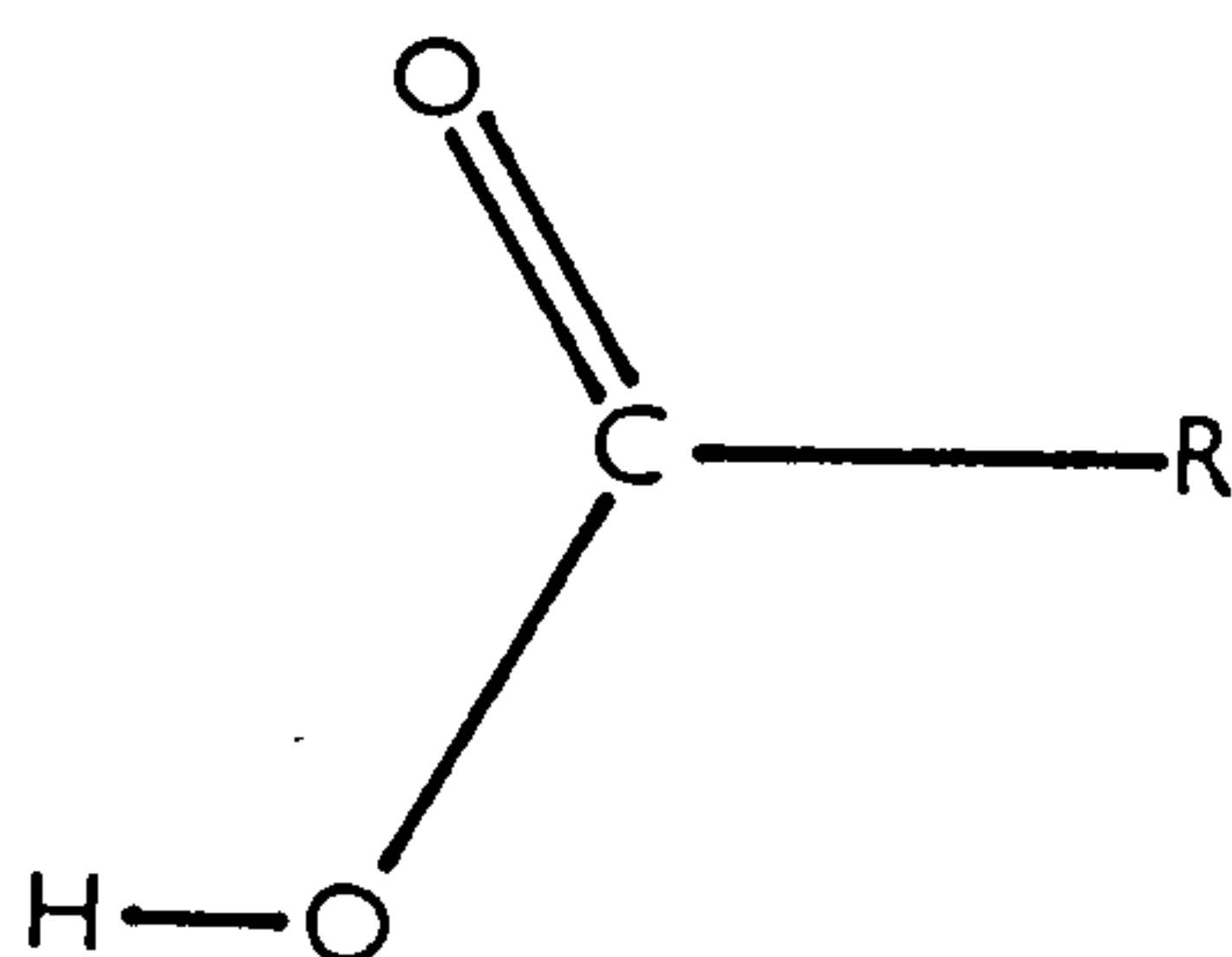
## TITANIUM CARBOXYLATES AND POLYMERISATION

A number of polymerisation catalysts use a titanium carboxylate species as the transition metal component. Some titanium carboxylate polymerisation catalysts predate Ziegler's original patent for the titanium tetrachloride/triethyl aluminium system. A selection of titanium carboxylate polymerisation catalysts is shown in Table 1.2.

## CARBOXYLIC ACIDS AND METAL CARBOXYLATES

### Carboxylic Acids

Monocarboxylic acids are defined as organic compounds containing one carboxyl (-COOH) group.<sup>(29)</sup> The carboxyl group may carry a range of other groups which influence the properties of the acid.



A Carboxylic acid.

The acidity of the carboxylic acid depends upon the degree of ionisation of the carboxyl group into a carboxylate anion and a hydrated proton.



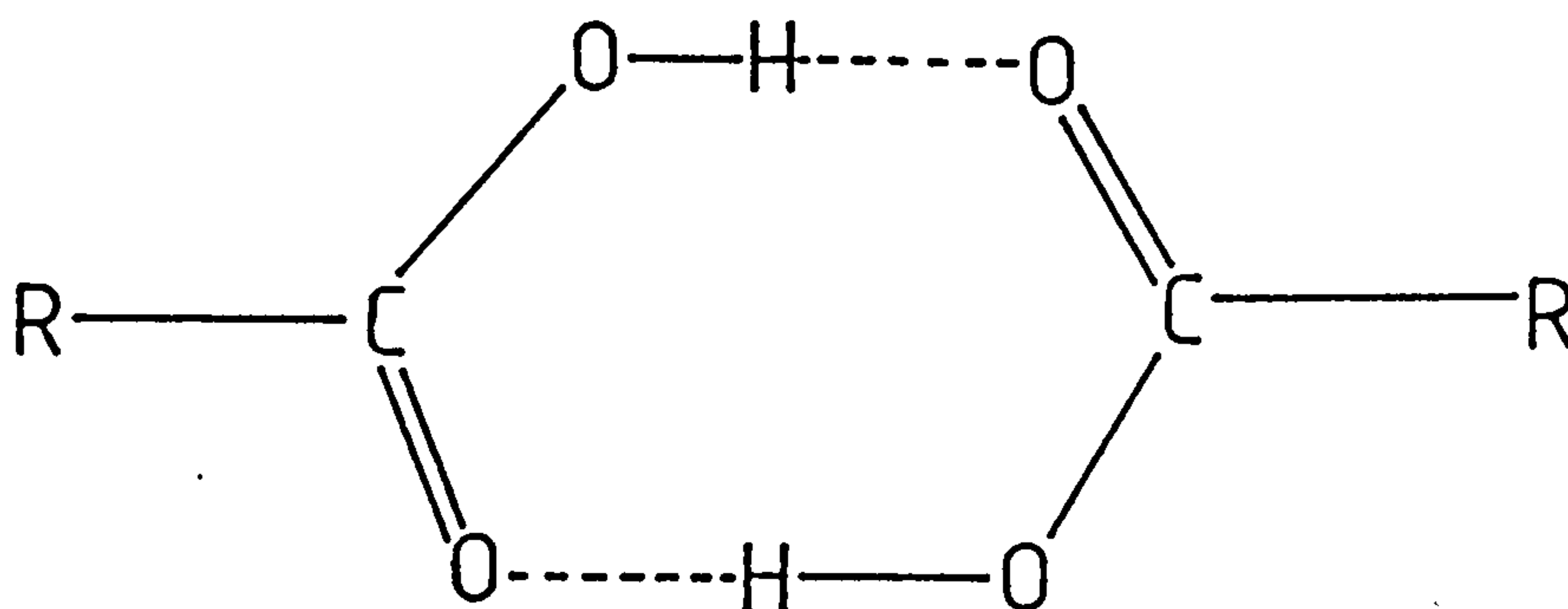
**Table 1.2 : Titanium Carboxylates as Polymerisation catalysts.**

Reference	Catalytic System	Monomer
Standard Oil Development Co. Brit. Pat. 578,888 (1946) CA <u>41</u> : P3478a	TiCl <sub>2</sub> (OAc) <sub>2</sub> (Friedel-Crafts type Catalyst)	-
"Montecatini" Ital.Pat. 578,728 (1958) CA <u>53</u> : P20913d	TiCl <sub>2</sub> (O <sub>2</sub> CR) <sub>2</sub> (R=CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> or C <sub>6</sub> H <sub>5</sub> ) with Et <sub>3</sub> Al	ethylene
Montecatini Edison Spa Ger.Offen. 2,013,730 (1970) CA <u>73</u> : 121062n	TiCl <sub>3</sub> (OBz) milled with MgCl <sub>2</sub> or MgBr <sub>2</sub> used with iso-Bu <sub>3</sub> Al	ethylene
Montecatini Edison Spa Fr.Pat. 2,103,071 (1970) CA <u>78</u> : 44266f	TiCl <sub>3</sub> (AcO) and 1:1 MgCl <sub>2</sub> :NaCl mixture used with iso-Bu <sub>3</sub> Al	ethylene
Maruzen Petrochemical Co.Ltd. Japan Kokai 72 34,587 (1972) CA <u>78</u> : 137026t	TiCl <sub>3</sub> (OBz) and Bu <sub>3</sub> Al in toluene	1-butene 1-hexene
Maruzen Petrochemical Co. Ltd. Japan Kokai 72 34,588 (1972) CA <u>79</u> : 79722z	TiCl <sub>3</sub> (OBz) or TiCl <sub>3</sub> (OAc) with iso-Bu <sub>3</sub> Al in toluene	Propylene 2,1-hexene 1,7 Octadiene (forms a co-polymer)
Maruzen Petrochemical Co.Ltd. Ger.Offen. 2,112,839 (1970) CA <u>76</u> : 47124c	SnCl <sub>4</sub> and TiCl <sub>3</sub> (OAc) with iso-Bu <sub>3</sub> Al in toluene	Propylene butadiene (forms a co-polymer)
Rafikov et al Izv. Akad. Navk. SSSR, Ser Khim 1975, 7, 1615-17 CA <u>83</u> : 193805m	TiCl <sub>2</sub> (RCO <sub>2</sub> ) <sub>2</sub> [R=CH <sub>3</sub> , CH <sub>2</sub> Cl CHCl <sub>2</sub> , CCl <sub>3</sub> or CF <sub>3</sub> ] with iso-Bu <sub>3</sub> Al	butadiene

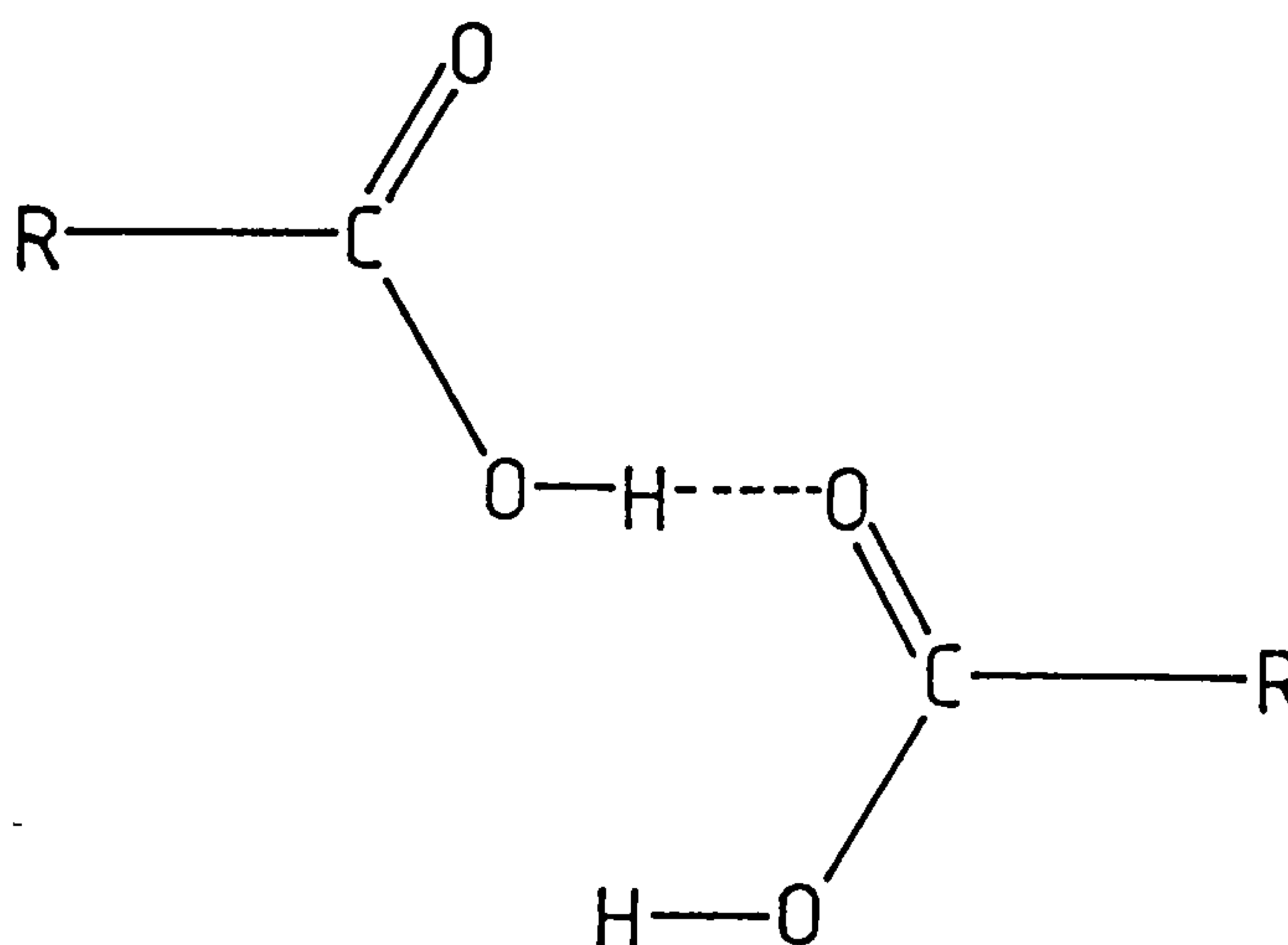


Acetic acid has a  $pK_a$  of 4.74, however if the acid contains an electron withdrawing group, then the carboxylate anion will be stabilised, and the  $pK_a$  lowered. If the acid contains an electron releasing group inductive effects will cause the acid to have a  $pK_a$  which is increased relative to that of acetic acid.

Carboxylic acids tend to dimerise due to intermolecular hydrogen bonding. In the solid state neutron diffraction measurements<sup>(30)</sup> show that the acids form a cyclic dimer while in aqueous solution an open dimeric form is preferred.<sup>(31)</sup>



Carboxylic acid cyclic dimer.



Carboxylic acid open dimer.

The carboxylate anion is symmetrical with two equal C-O bonds 1.26Å long. The O-C-O bond angle is in the range 125-130°. Resonance stabilisation is responsible for the symmetry of the carboxylate anion.

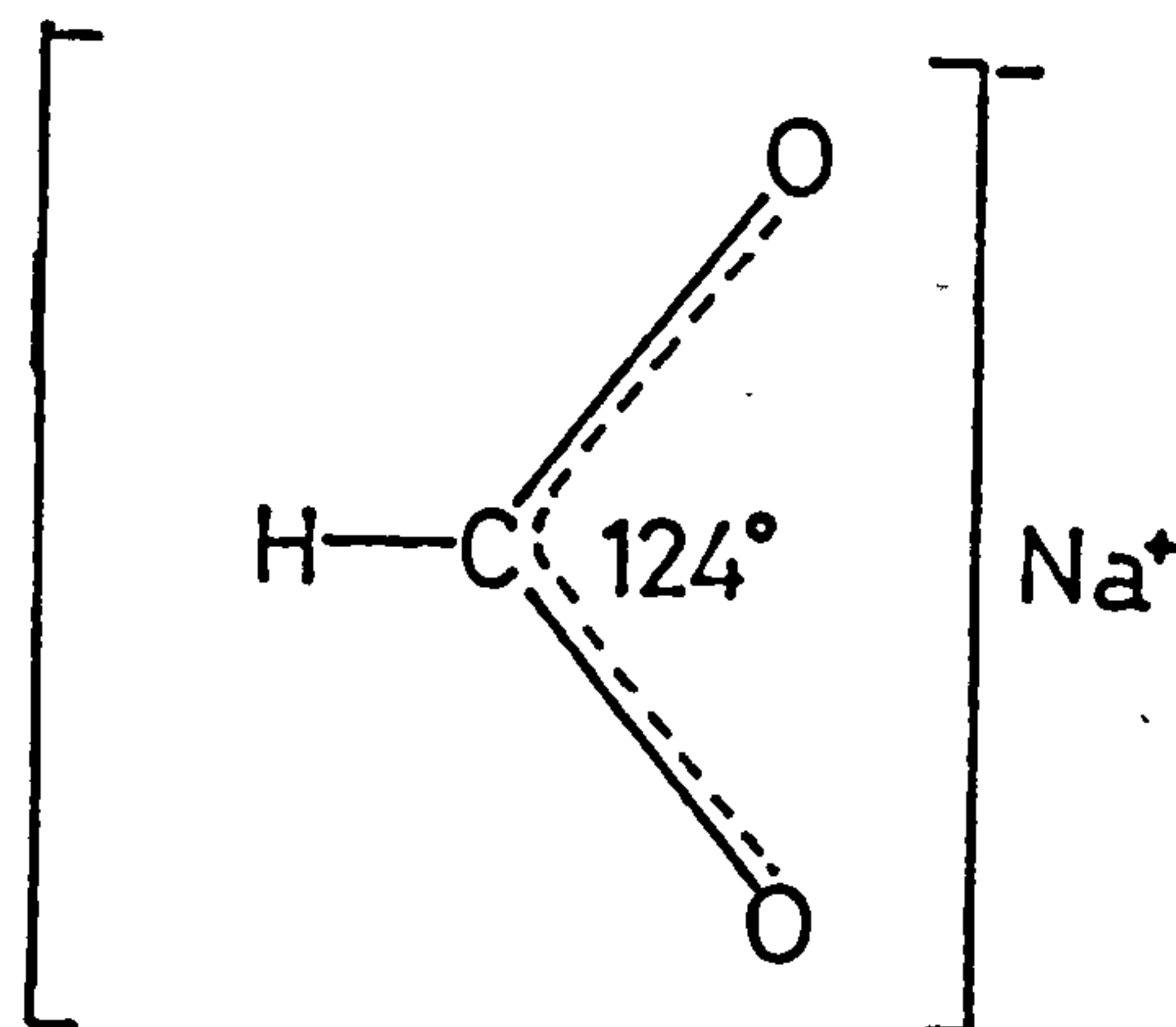
## CARBOXYLATE COORDINATION MODES

Carboxylate anions may coordinate to metals in many different ways. The large number of different carboxylate structures may be explained by considering the main bonding modes and the possibility of a carboxylate using two or more bonding modes at once.

The main carboxylate coordination types are discussed below:

(i) **Ionic**

e.g.  $[\text{Na} (\text{O}_2\text{CH})]_{32}$

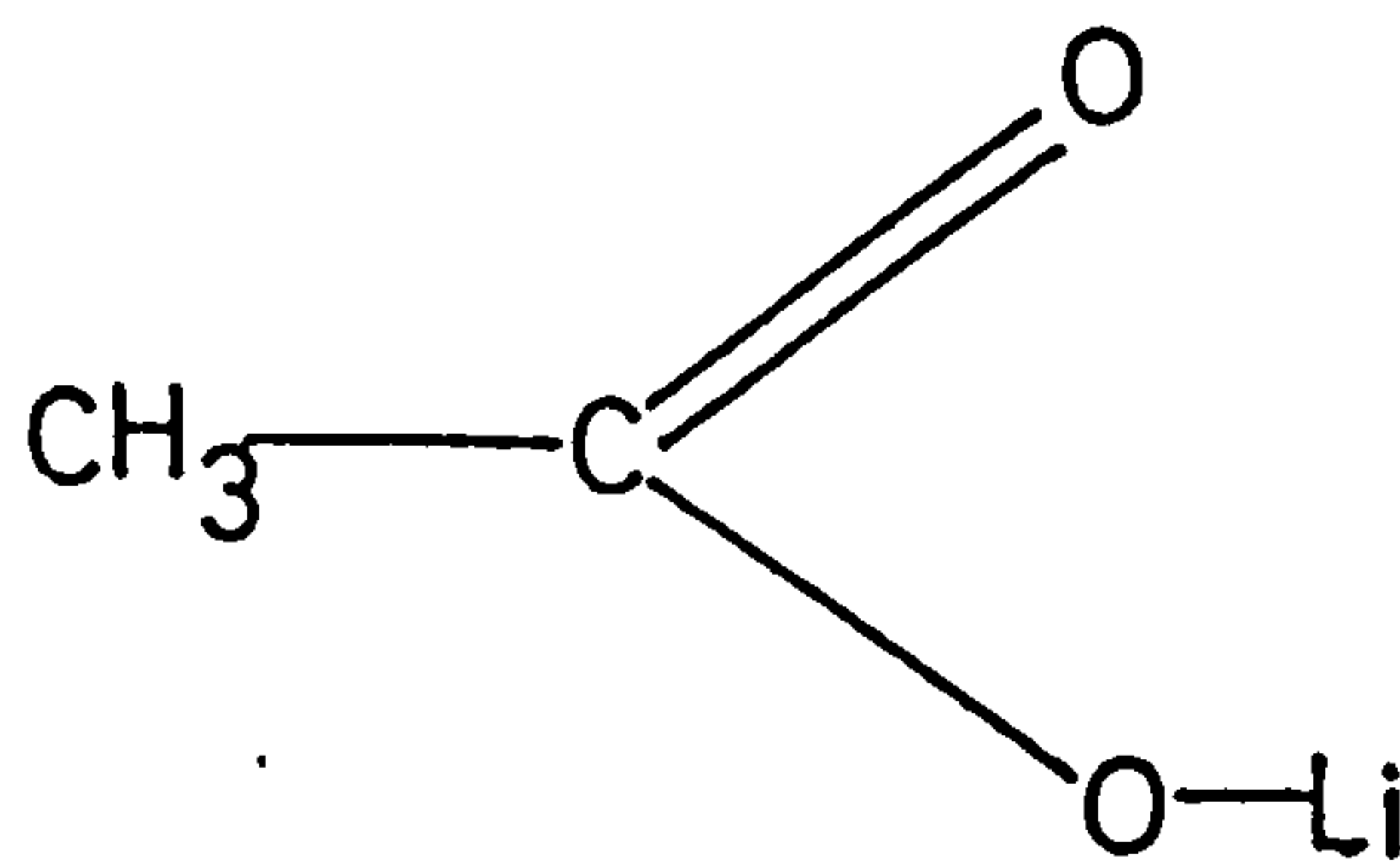


It appears that there is little cation-anion interaction in the carboxylates of elements such as Na or K so these carboxylates are considered to be ionic with two equal C-O bonds in the carboxylate anion(33).

(ii) **Unidentate**

e.g.  $[\text{C}_6\text{H}_5\text{Hg} (\text{O}_2\text{CCH}_3)]_{34}$

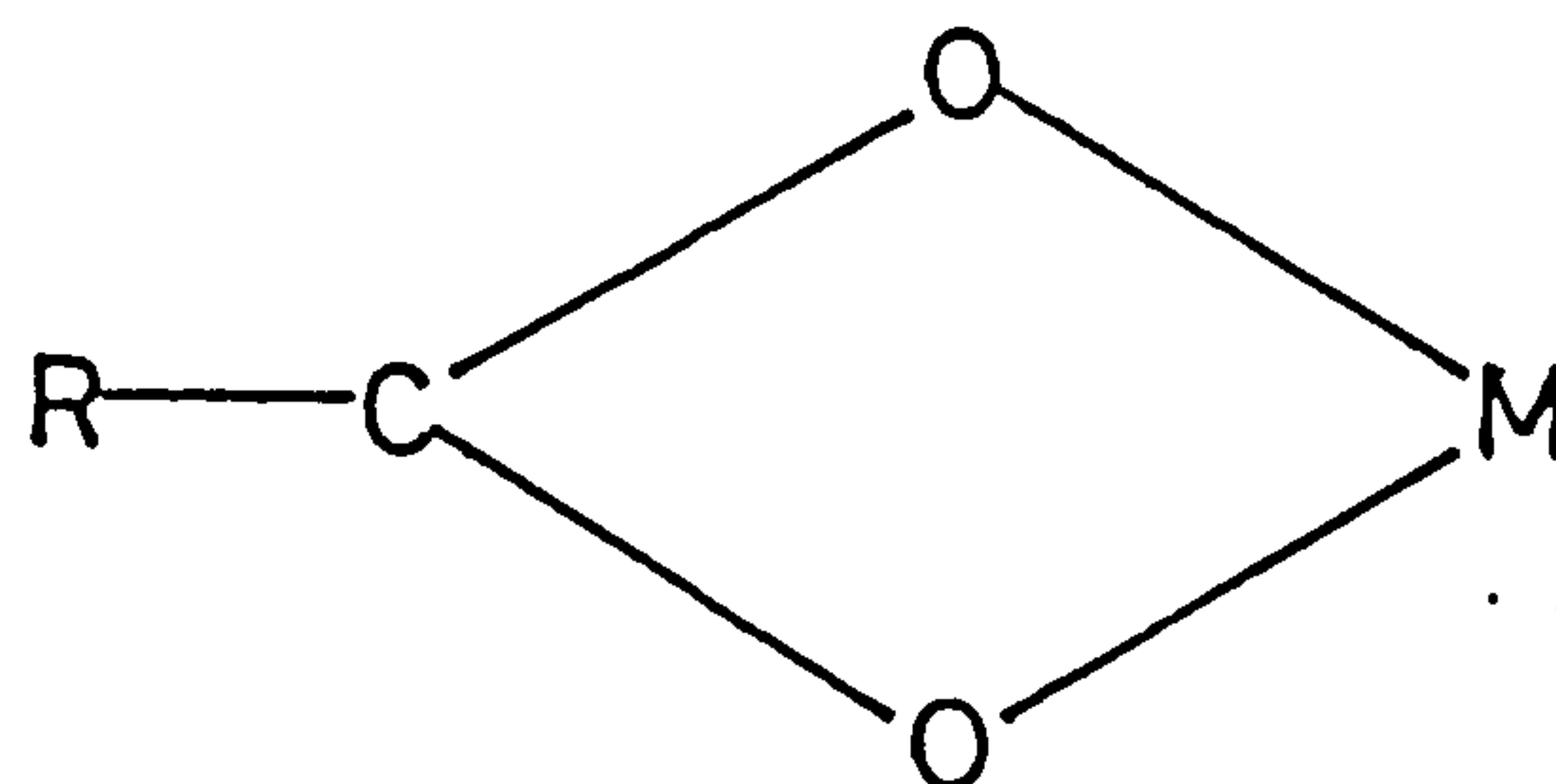
$[(\text{Cyclo-C}_6\text{H}_{11})_3\text{Sn}(\text{O}_2\text{CCH}_3)]_{35}$



The anion bonds to the metal through one oxygen resulting in a pseudo-ester configuration with unequal C-O bond lengths.

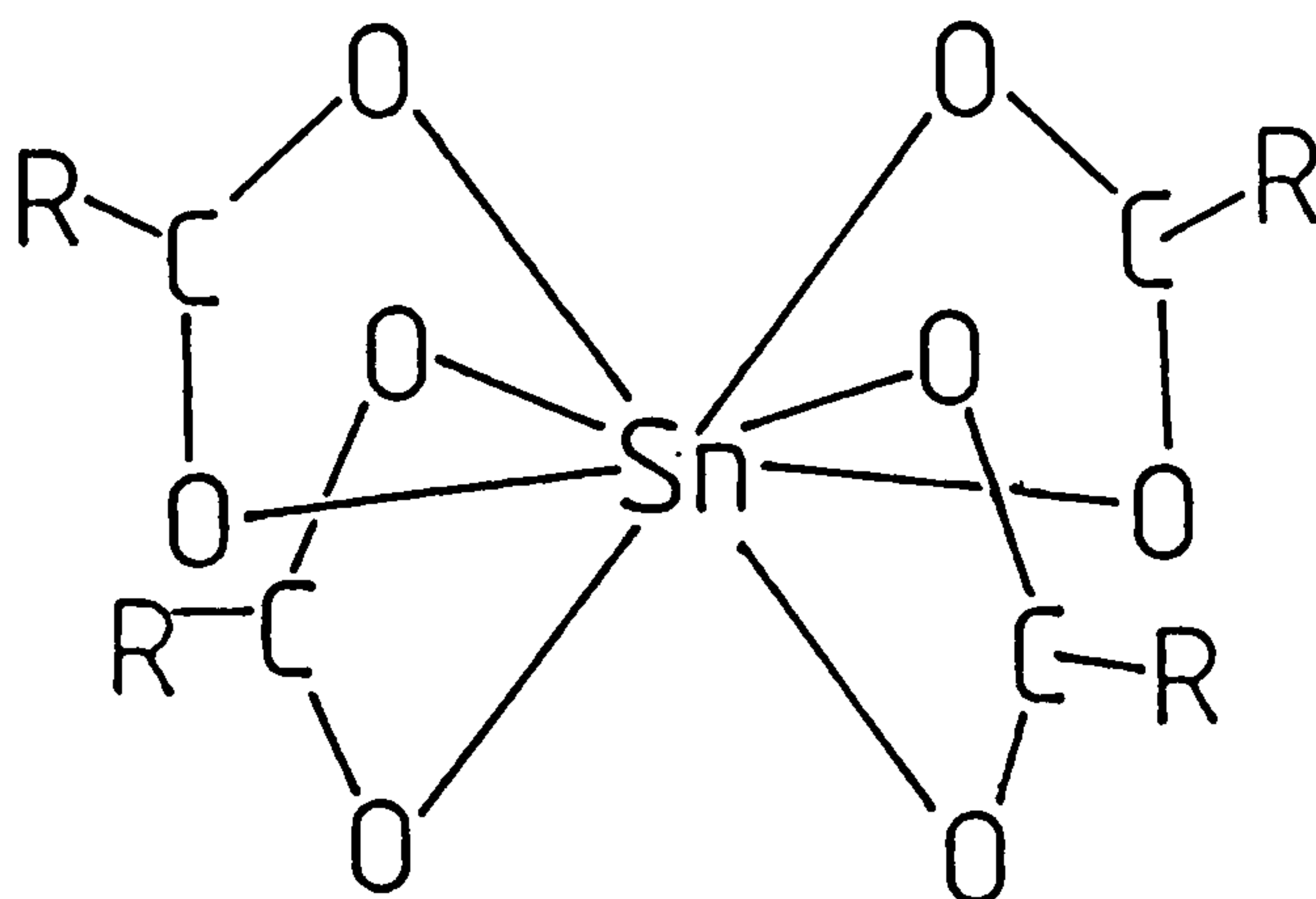
(iii) Bidentate chelating

e.g.  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{O}_2\text{CCMe}_3)]^{36)}$   
 $[\text{Hg}(\text{O}_2\text{CCH}_3)_2(\text{Bu}_3\text{P})]^{37)}$



The few confirmed examples of bidentate chelating carboxylate anions seem to indicate that this mode occurs mainly due to steric interactions.

In  $\text{Sn}(\text{O}_2\text{CCH}_3)_4$  three of the acetate ions are bidentate symmetrical chelating but steric crowding around the tin atom prevents the coordination of eight ligand atoms, so one ion is a bidentate unsymmetrical chelating group with one Sn-O bond longer than the other<sup>(38)</sup>



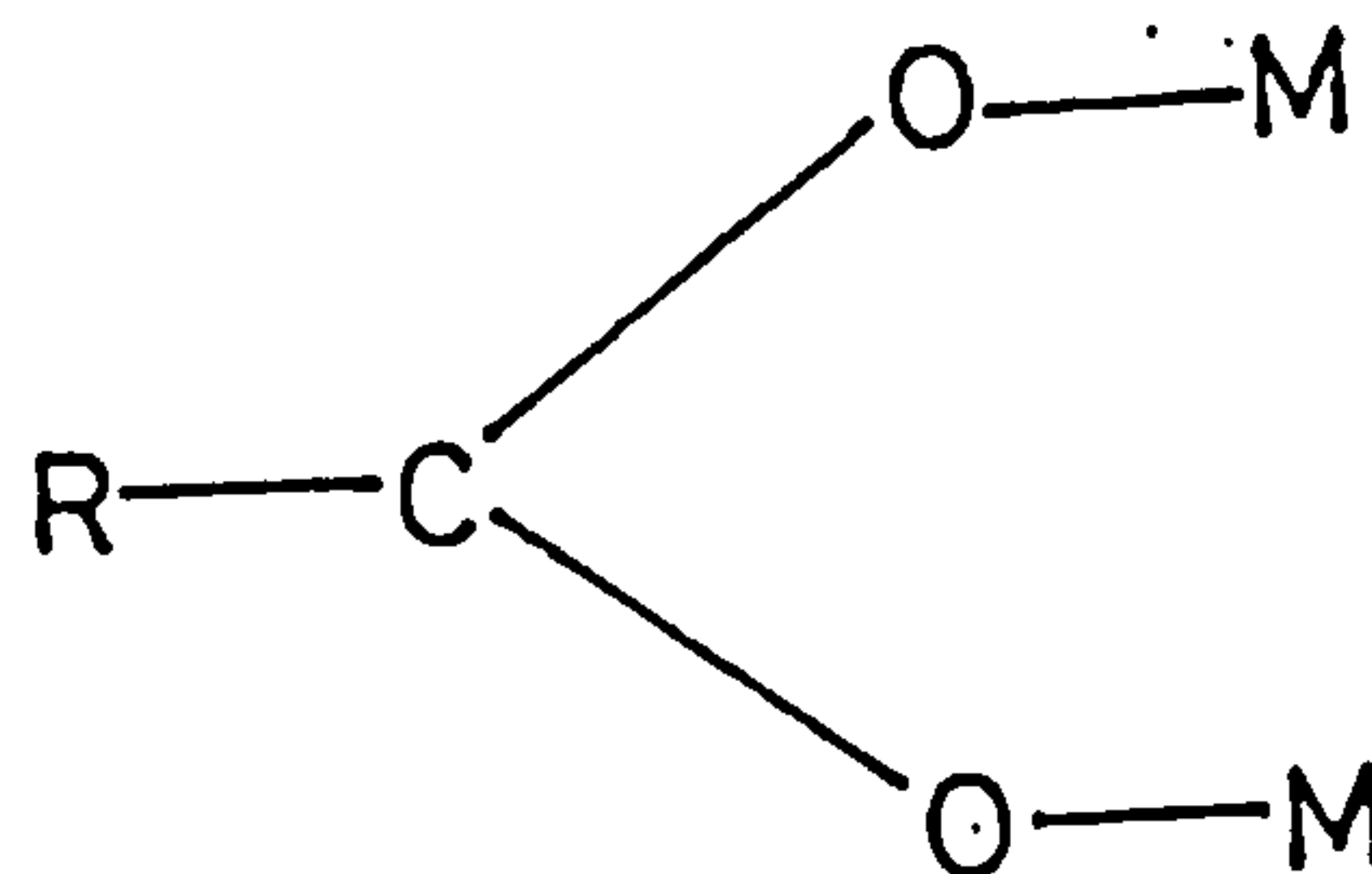
$[\text{Sn}(\text{O}_2\text{CCH}_3)_4]$

#### (iv) Bidentate bridging

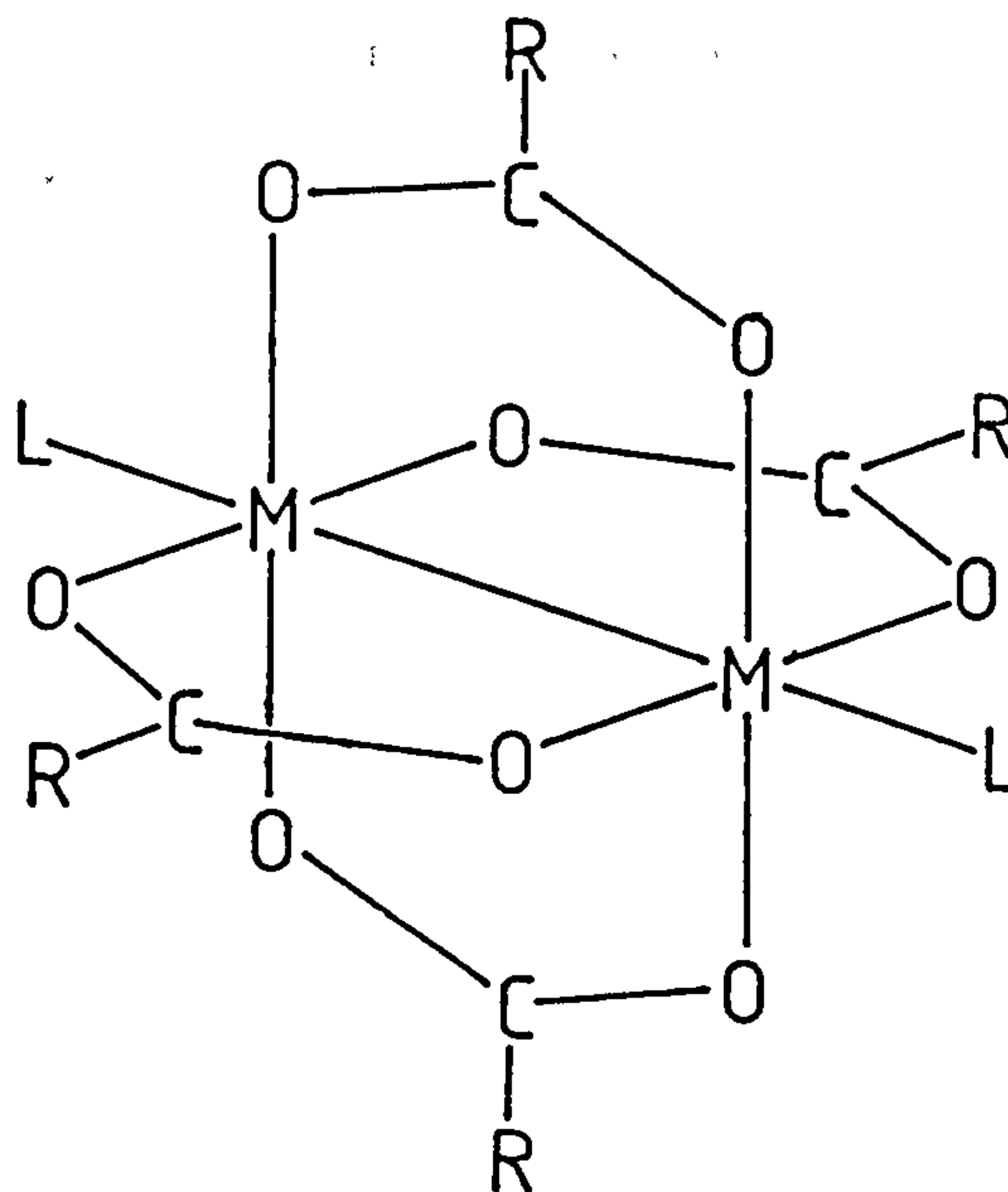
Carboxylate anions readily form bidentate bridges giving oligomeric or polynuclear species. Four types of carboxylate bridges have been identified.

##### Syn-Syn\*

e.g.  $[\text{Ru}_2(\text{O}_2\text{CC}_3\text{H}_7)_4\text{Cl}]^{40}$   
 $[\text{Mo}_2(\text{O}_2\text{CCH}_3)_4]^{41}$



Syn-Syn bridges allow the metal atoms to approach close enough for bonding interactions to occur.



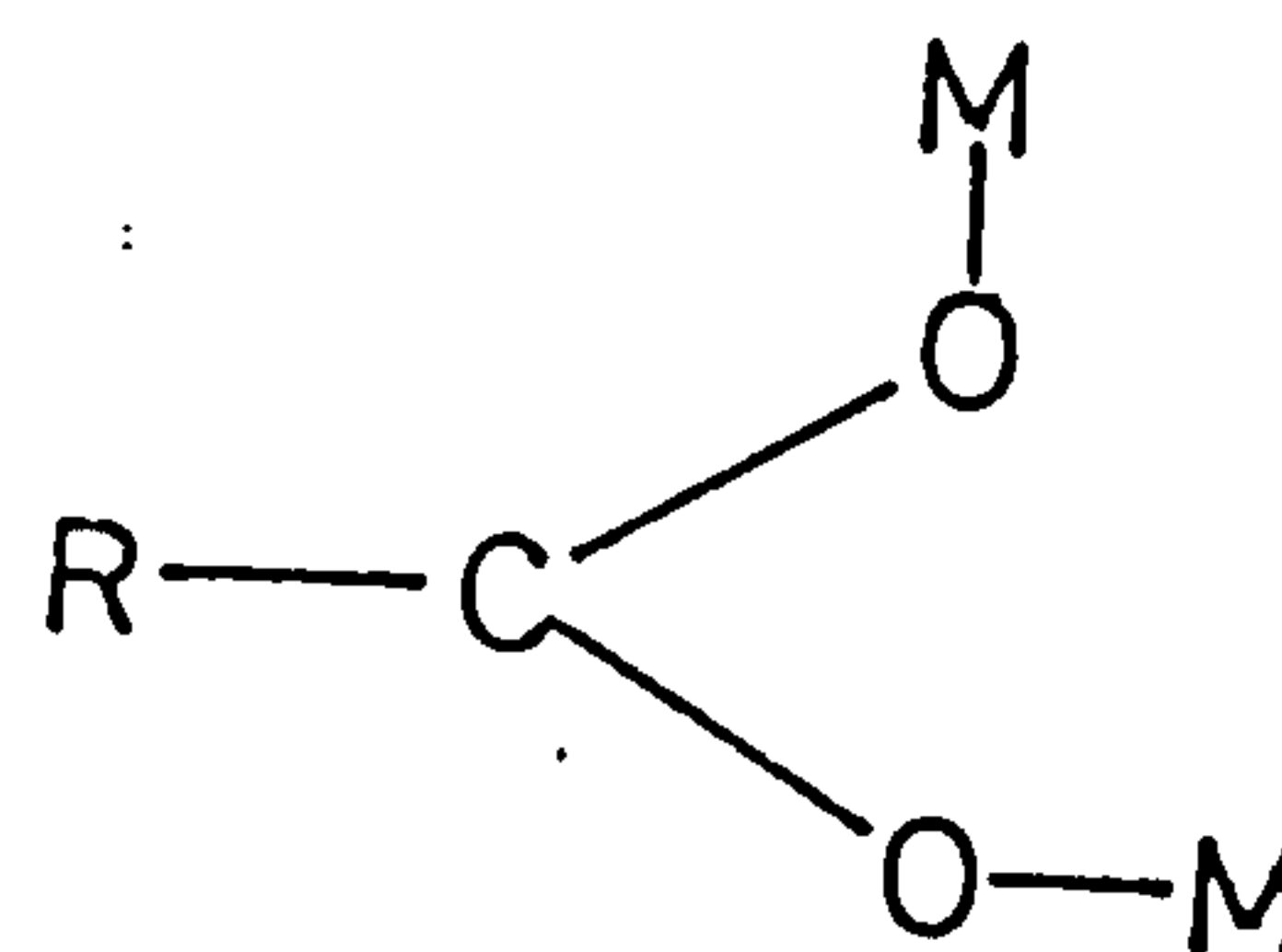
$[\text{M}_2(\text{O}_2\text{CR})_4]$

\*See Appendix 1.

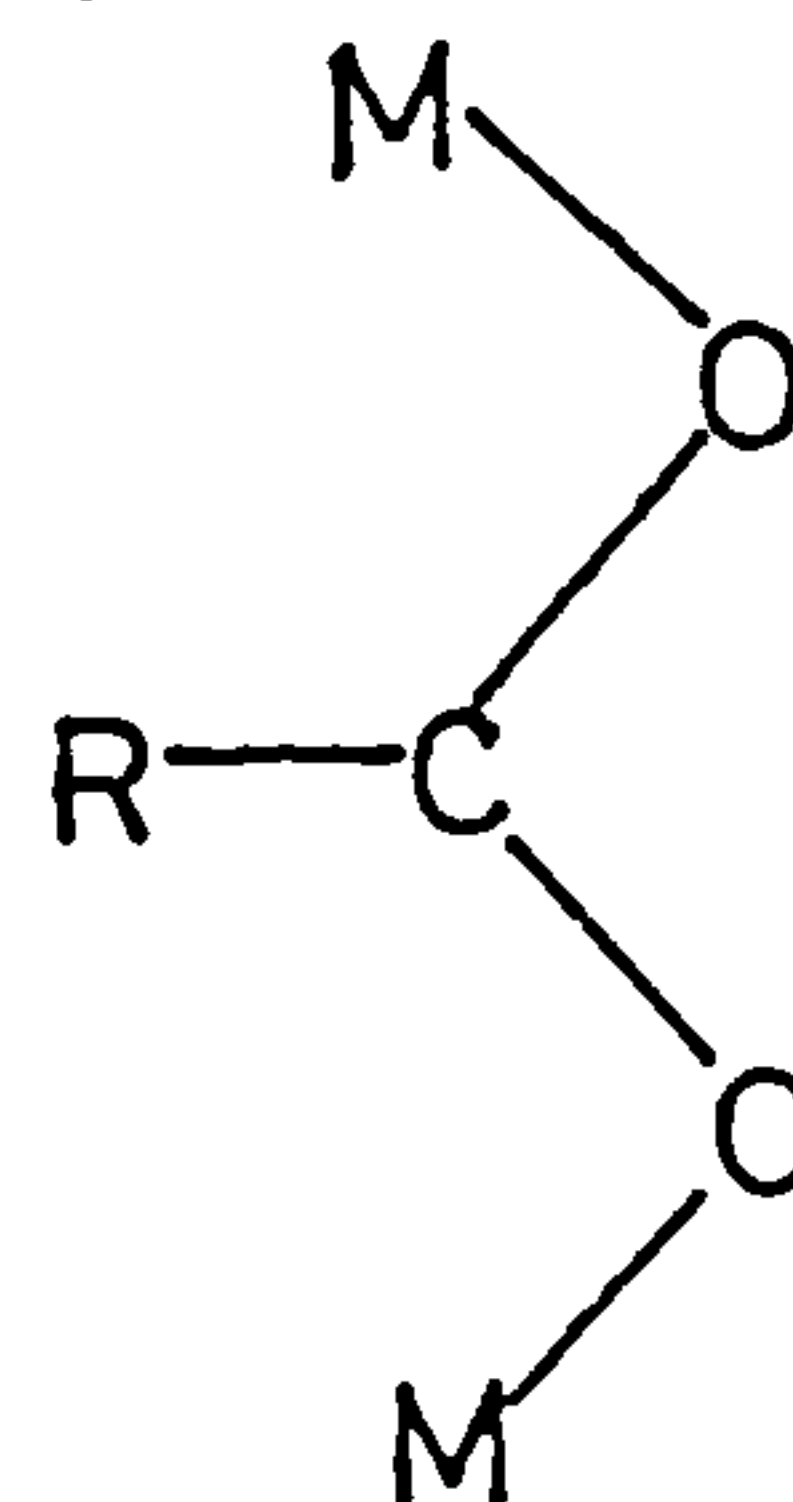


**Anti-Syn**

e.g.  $[\text{Cu}(\text{O}_2\text{CCH}_3)_2]^{42)}$   
 $[\text{Me}_3\text{Sn}(\text{O}_2\text{CCH}_3)]^{43)}$

**Anti-Anti**

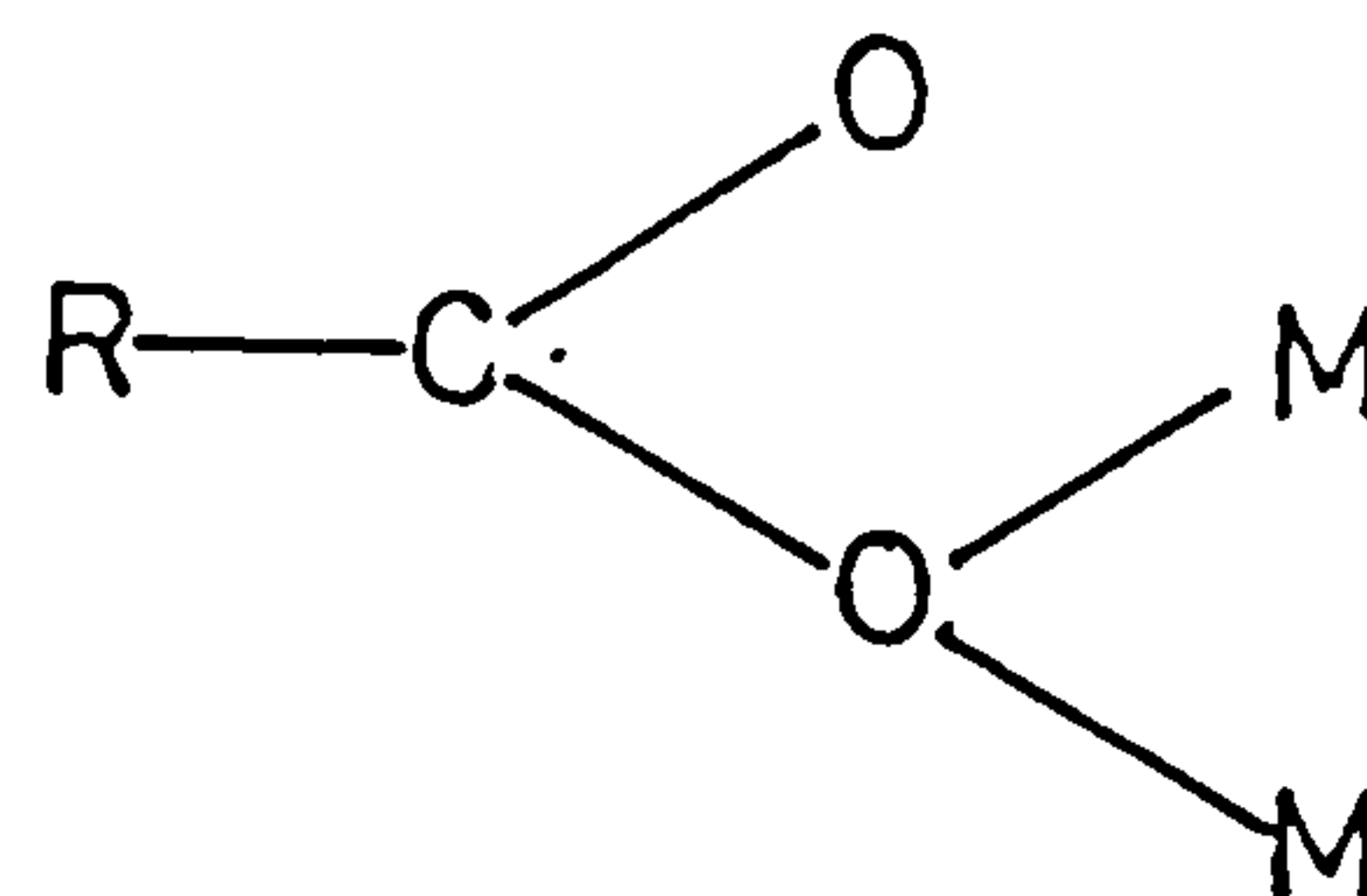
e.g.  $[\text{Mn}(\text{O}_2\text{CCH}_3)_2(\text{H}_2\text{O})_4]^{44)}$



In complexes which only contain these types of bridges metal-metal bonding interactions do not occur.

**Monatomic**

e.g.  $[\text{Hg}(\text{O}_2\text{CCH}_3)_2[(\text{cyclo-C}_6\text{H}_{11})_3\text{P}]]^{45)}$   
 $[\text{Cu}(\text{O}_2\text{CCH}_3)]^{46)}$

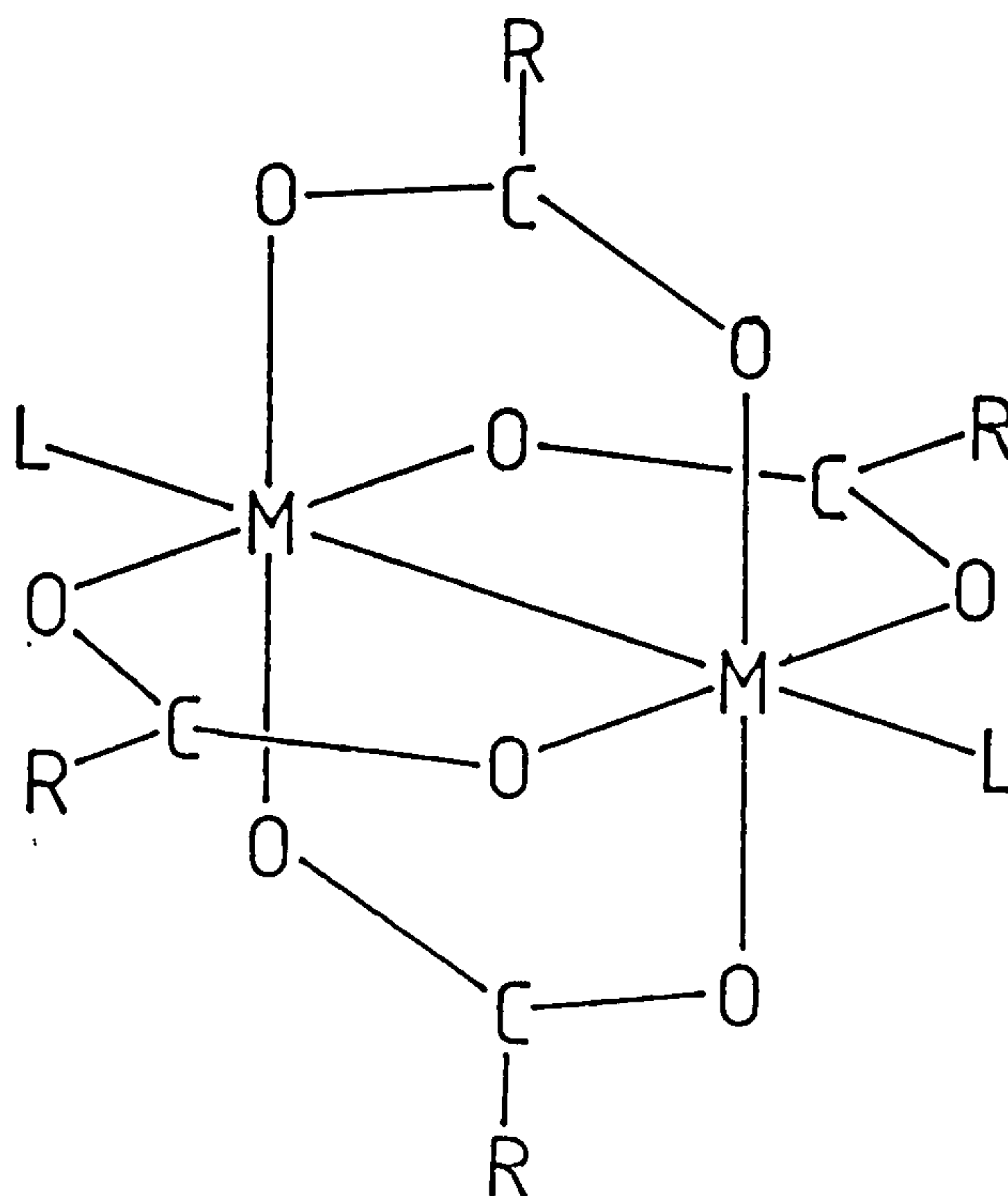


The non-monatomically bridging oxygen atom of the anion may interact with one of the metal atoms being bridged or with a different metal atom. In  $\text{Cu}(\text{O}_2\text{CH}_3)$  it forms a syn-syn bridge to another copper(46).

## OLIGOMERIC METAL CARBOXYLATES

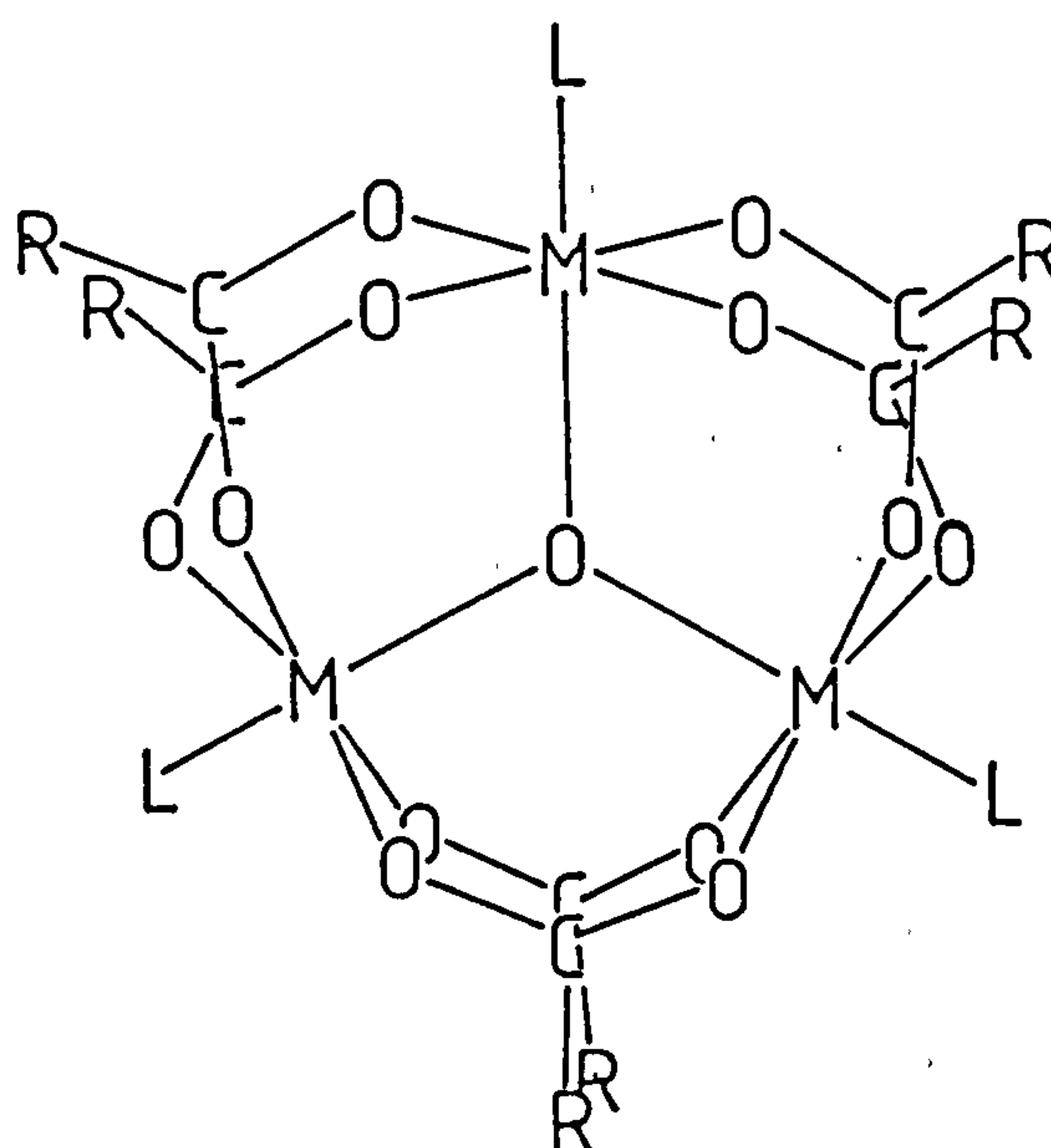
The various bonding modes of the carboxylate anion allow the formation of multinuclear oligomeric species connected together by carboxylate bridges.

Dimers are most common for the +2 state of metals,  $\text{M}_2(\text{O}_2\text{CR})_4$  species being known for (Cr, Mo, W, Rh, Cu)(47) and Zn(51). These species have the general structure:

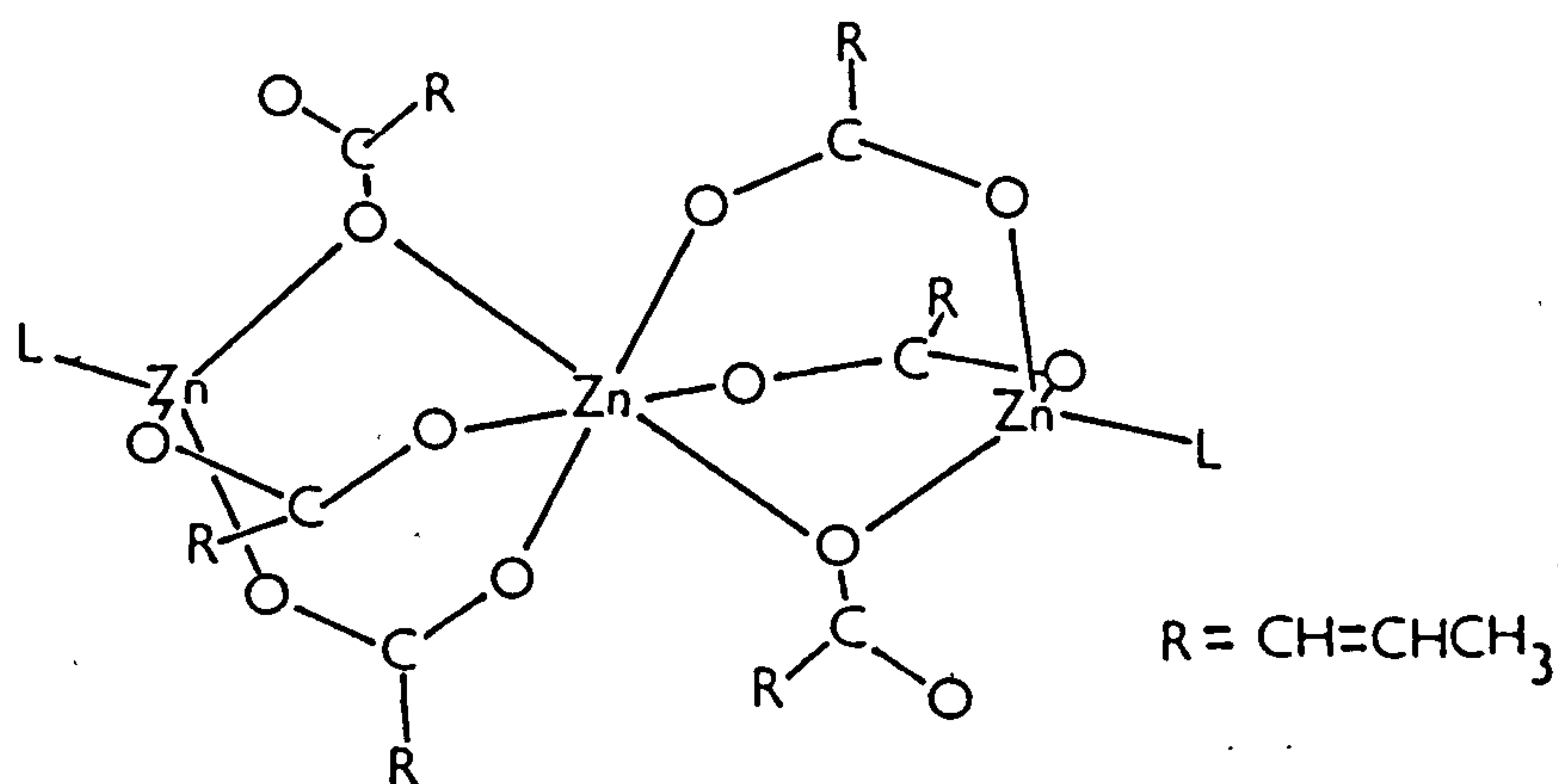


Some dimers occur for other oxidation states e.g.  $\text{Re}_2(\text{O}_2\text{CR})_4 \text{Cl}_2$  which is Re(III)(48) and  $\text{Os}_2(\text{O}_2\text{CCH}_3)_2(\text{CO})_6$  which is Os (I)(49).

Many trimeric metal carboxylates are known(50). Most of these have the trinuclear structure shown below. The three metal atoms are arranged in a triangle with bridging carboxylates and a central oxygen atom. This structure is common for M(III) carboxylates.



An alternative trimetal structure is linear as found in  $[\text{Zn}_3(\text{CH}_3\text{CH}=\text{CHCO}_2)_6 (\text{C}_9\text{H}_7\text{N})_2]$ (51). This complex contains four bidentate and two monodentate carboxylate ligands with two terminal quinoline ligands



Tetramers are not as common but are found for Pt(II)(52), Zn(53) and Co(54). The zinc and cobalt structures are similar to that of  $\text{Be}_4\text{O}(\text{O}_2\text{CH}_3)_6$ . The

platinum structure contains a metal-metal bonded square cluster of platinum atoms with 4 *syn-syn* carboxylate ligands in the plane of the cluster and 4 alternately above and below it.

Some polymeric carboxylates exist notably  $\text{Me}_3\text{Sn}(\text{O}_2\text{CH})$  which forms long molecular chains with bridging formate groups(55).

## IDENTIFICATION OF CARBOXYLATE BONDING MODE

It is difficult to distinguish between the different types of carboxylate coordination. The only techniques which are applicable being diffraction methods, and vibrational spectroscopy.

The coordination type cannot be determined by examination of the number of infra-red or Raman vibrations due to the low symmetry of carboxylate anions. Attempts have been made to relate the bonding mode to the values of C-O stretching frequencies.

The bonds used in attempts to relate bonding mode to vibrational spectra are usually the  $\text{CO}_2^-$  symmetric stretch ( $\nu_3$ ) and the  $\text{CO}_2^-$  asymmetric stretch ( $\nu_8$ ). However even for relatively simple carboxylate ions, the asymmetric stretch also contains some carboxylate rocking mode and the symmetric stretch has contributions from any methyl deformations present as well as from carboxylate deformation and carbon-carbon stretching modes. When the carboxylate anion coordinates to a metal the symmetric and asymmetric bonds will shift.

Rigorous bond assignments have only been performed for the acetate<sup>(56)</sup> and formate<sup>(56)</sup> carboxylate anions. Therefore assignments of  $\nu(\text{CO}_2^-)_{\text{asym}}$  and  $\nu(\text{CO}_2^-)_{\text{sym}}$  for other carboxylates may be less accurate.

Two methods of using infra-red spectroscopy to determine carboxylate bond mode have been proposed:

### (i) Difference of Carboxylate Stretching Frequencies ( $\Delta$ ) Method

The carboxylate anion contains two equivalent oxygen atoms for all bonding modes apart from unidentate. In the case of unidentate coordination the oxygen atoms become inequivalent. This causes  $\nu(\text{CO}_2^-)_{\text{asym}}$  to increase,  $\nu(\text{CO}_2^-)_{\text{sym}}$  to decrease and the separation between the two ( $\Delta$ ) to increase. It has been proposed<sup>(58,57)</sup> that  $\Delta$  values considerably larger than the ionic value (e.g.  $\Delta$  for sodium acetate =  $223\text{cm}^{-1}$ ) indicate unidentate coordination. Carboxylates with a  $\Delta$  value less than that for ionic carboxylates were supposed<sup>(57)</sup> to be chelating or bridging.

### (ii) Shift from Ionic Values Method

Manhas and Trikha<sup>(58)</sup> proposed that the type of carboxylate coordination could be related to the shift of the  $\nu(\text{CO}_2^-)$  bonds relative to the ionic case.

However a recent paper<sup>(59)</sup> has shown that this approach is completely invalid except for the unidentate case. For the unidentate case this criterion is merely a restatement of the  $\Delta$  method.



The conclusion of the recent reviews (57,59) was that the only bonding mode definitely detectable by infra-red measurements is the unidentate mode. In some cases chelating and/or bridging modes may be detected by infra-red methods.

## GENERAL TITANIUM CHEMISTRY

This section is not intended to be a comprehensive review of titanium compounds. Many books and reviews are available, thus only general features are presented for introductory purposes.

Titanium is the first d-block transition element in the periodic table. It has four valence electrons in the configuration  $3d^2 4s^2$ . The most common oxidation state is titanium (IV). Less stable oxidation states are -I, 0, II and III; these states are readily oxidized to titanium (IV). As the energy for removal of all four valence electrons is high the  $Ti^{4+}$  ion does not exist and titanium (IV) compounds are mainly covalent.

## LOW VALENT TITANIUM COMPLEXES

Few compounds are known for the -I, 0, and II oxidation states. The 0 and -I states occur in the complexes  $Ti(bipy)_3$  and  $Li[Ti(bipy)_3]$  prepared by Herzog and coworkers (61). Dimethylformamide forms a grey-green complex with  $TiCl_2$  (62). A range of complexes, general formula  $TiCl_2 \cdot 2L$  ( $L = CH_3CN, C_4H_8O, C_5H_{10}O$ , pyridine, bipy and phen), have been synthesized (63). These complexes are reported to have six coordinate polymeric structures.

## TITANIUM (III)

Titanium (III) forms a wide range of complexes with many different stoichiometries such as  $[\text{ML}_6]^{3+} 3\text{X}^-$ ,  $[\text{ML}_4\text{X}_2]^+ \text{X}^-$ ,  $[\text{ML}_3\text{X}_3]$ ,  $[\text{ML}_2\text{X}_3]$ ,  $\text{R}^+ [\text{ML}_2\text{X}_4]^-$  and  $(\text{R}^+)_3 [\text{MX}_6]^{3-}$  where L = monodentate ligand, X = a halide and R = monovalent cation. There are also compounds with bi- and terdentate ligands coordinated to the titanium (III) centre.

In aqueous dilute acid solution the  $\text{Ti}^{3+}$  ion exists as  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  but the crystalline hexahydrates of titanium trichloride and tribromide exist as  $[\text{Ti}(\text{H}_2\text{O})_4\text{X}_2]\text{X} \cdot 2\text{H}_2\text{O}$ . This stoichiometry also occurs when  $\text{TiCl}_3$  is dissolved in an alcohol,  $(\text{Ti}(\text{alcohol})_4\text{Cl}_2)^+ \text{Cl}^-$  being formed(64).

Neutral  $[\text{ML}_3\text{X}_3]$  complexes are very common. They are normally prepared by refluxing the titanium trihalide in an appropriate ligand. Ligands used include THF, dioxan, acetone, formamide, acetonitrile, pyridine and  $\gamma$ -picoline.

Complexes with the  $[\text{ML}_2\text{X}_3]$  stoichiometry are five coordinate. An X-ray investigation of  $\text{TiBr}_3 \cdot 2\text{NMe}_3$  has shown that the complex has a trigonal bipyramidal structure with the ligands occupying the axial positions(65).

Reaction of  $[\text{TiCl}_3 \cdot 3\text{MeCN}]$  with tetraethylammonium chloride or bromide gives the complexes  $\text{Et}_4\text{N} [\text{TiCl}_4 \cdot 2\text{MeCN}]$  or  $\text{Et}_4\text{N} [\text{TiCl}_3 \cdot \text{Br} \cdot 2\text{MeCN}]$  respectively(66). The salt  $(\text{pyH})_3 [\text{TiCl}_6]$  may be isolated from the reaction between  $[\text{TiCl}_3 \cdot 3\text{MeCN}]$  and pyridinium chloride(66).

With bidentate ligands (B) such as acetylacetone and its variants titanium trichloride forms strongly coloured complexes with the general formula  $TiB_3$ (67). Two types of complex are formed with neutral bidentate ligands. One type has the structural formula  $[TiB_3]X_3$  and the other  $[TiCl_2B_2]$   $[TiCl_4B]$ . Dimethoxyethane forms complexes of the type  $[TiBr_2(C_4H_{10}O_2)_2]$   $[TiBr_4(C_4H_{10}O_2)]$  with titanium tribromide(68).

Titanium trichloride forms a dark green 1:1 adduct on reaction with 2,2',2'', - terpyridyl(64). It is probably an octahedral monomer.

## TITANIUM (IV)

The chemistry of titanium (IV) has been much investigated and is now well established. Most work has concerned the synthesis of titanium tetrachloride adducts using neutral ligands. The titanium atom in these adducts may be five, six, seven or eight coordinated depending upon the ligand. A common feature of the chemistry of titanium tetrahalides is reaction with a ligand by elimination of hydrogen halide.

The titanium halides all behave as Lewis acids. Titanium tetrafluoride is a white solid. Its lack of solubility in non-polar solvents implies it is a fluorine bridged polymer. The tetra-fluoride forms adducts with nitriles, ketones, alcohols, amines and aldehydes. These adducts have the general formula  $TiF_4 \cdot 2L$  or  $TiF_4 \cdot L$ . Fluorine NMR experiments suggest that the  $TiF_4 \cdot 2L$  species have octahedral geometry with the ligands cis to each other(69). The 1:1 amine complexes are thought to be fluorine bridged polymers(69).

Titanium tetrabromide is an orange crystalline solid which behaves as a covalent monomer in non-polar solvents. It forms adducts with neutral ligands of the types  $\text{TiBr}_4 \cdot \text{B}$  and  $\text{TiBr}_4 \cdot 2\text{L}$  (B = bidentate ligand, L = monodentate ligand). Phosphine and amine ligands cause reduction to  $\text{Ti(III)}$  but complexes with ethers such as tetrahydrofuran are stable(71).

Titanium tetraiodide is a dark brown solid. Its solid state structure consists of molecular lattices of tetrahedral units. Few complexes of  $\text{TiI}_4$  have been reported.  $\text{TiI}_4$  reacts with most ligands but the products have rarely been characterised.

Titanium tetrachloride is a colourless liquid (m.p.  $-23^\circ\text{C}$ , b.p.  $136^\circ\text{C}$ ). It fumes strongly in moist air, and reacts vigorously with water forming  $\text{TiO}_2$ .  $\text{TiCl}_4$  has four coordinate tetrahedral geometry. The Ti-Cl bonds are covalent in nature. It is possible that the titanium (IV) achieves an 18 electron configuration by being involved in  $\Pi$  bonding between filled chlorine orbitals and empty titanium 3d orbitals.

There is a huge number of titanium tetrachloride adducts with neutral ligands. The tetrachloride is known to form adducts with nitrogen, oxygen, phosphorus, arsenic and sulphur donor ligands. These adducts are of the form  $\text{TiCl}_4 \cdot 2\text{L}$ ,  $\text{TiCl}_4 \cdot \text{L}$  or  $\text{TiCl}_4 \cdot \text{B}$  (L = monodentate ligand, B = bidentate ligand). Some properties of selected titanium tetrachloride adducts are shown in Tables 1.3, 1.4 and 1.5.

The  $\text{TiCl}_4 \cdot 2\text{L}$  type adducts are generally octahedrally coordinated with the ligands cis to each other(69). The X-ray structure of  $\text{TiCl}_4 \cdot 2\text{POCl}_3$  shows this geometry(81). The  $\text{TiCl}_4 \cdot \text{B}$  adducts also have octahedral geometry.



**TABLE 1.3 ADDUCTS OF TITANIUM TETRACHLORIDE OF THE TYPE  $\text{TiCl}_4 \cdot 2\text{L}$** 

Ligand	Donor atom	Complex	Colour	M.p/ $^{\circ}\text{C}$	Ref.
Tetrahydrofuran	O	$\text{TiCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$	yellow	122-124 dec	64
Benzophenone	O	$\text{TiCl}_4 \cdot 2(\text{C}_6\text{H}_5)_2\text{CO}$	yellow	150	64
Acetonitrile	N	$\text{TiCl}_4 \cdot 2\text{CH}_3\text{CN}$	yellow	80 sub	64
Pyridine	N	$\text{TiCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$	yellow	190 dec	73
Triphenylphosphine	P	$\text{TiCl}_4 \cdot 2(\text{C}_6\text{H}_5)_3\text{P}$	red/black	149-151	64
Triethylphosphine	P	$\text{TiCl}_4 \cdot 2(\text{C}_2\text{H}_5)_3\text{P}$	dark red	144.5-148	64
1, 4 Thioxan	S	$\text{TiCl}_4 \cdot 2\text{C}_4\text{H}_8\text{S}$	yellow	-	70
Dimethylsulphide	S	$\text{TiCl}_4 \cdot 2(\text{CH}_3)_2\text{S}$	orange	95 - 99	64
Triphenylarsine	As	$\text{TiCl}_4 \cdot 2(\text{C}_6\text{H}_5)_3\text{As}$	purple	-	70

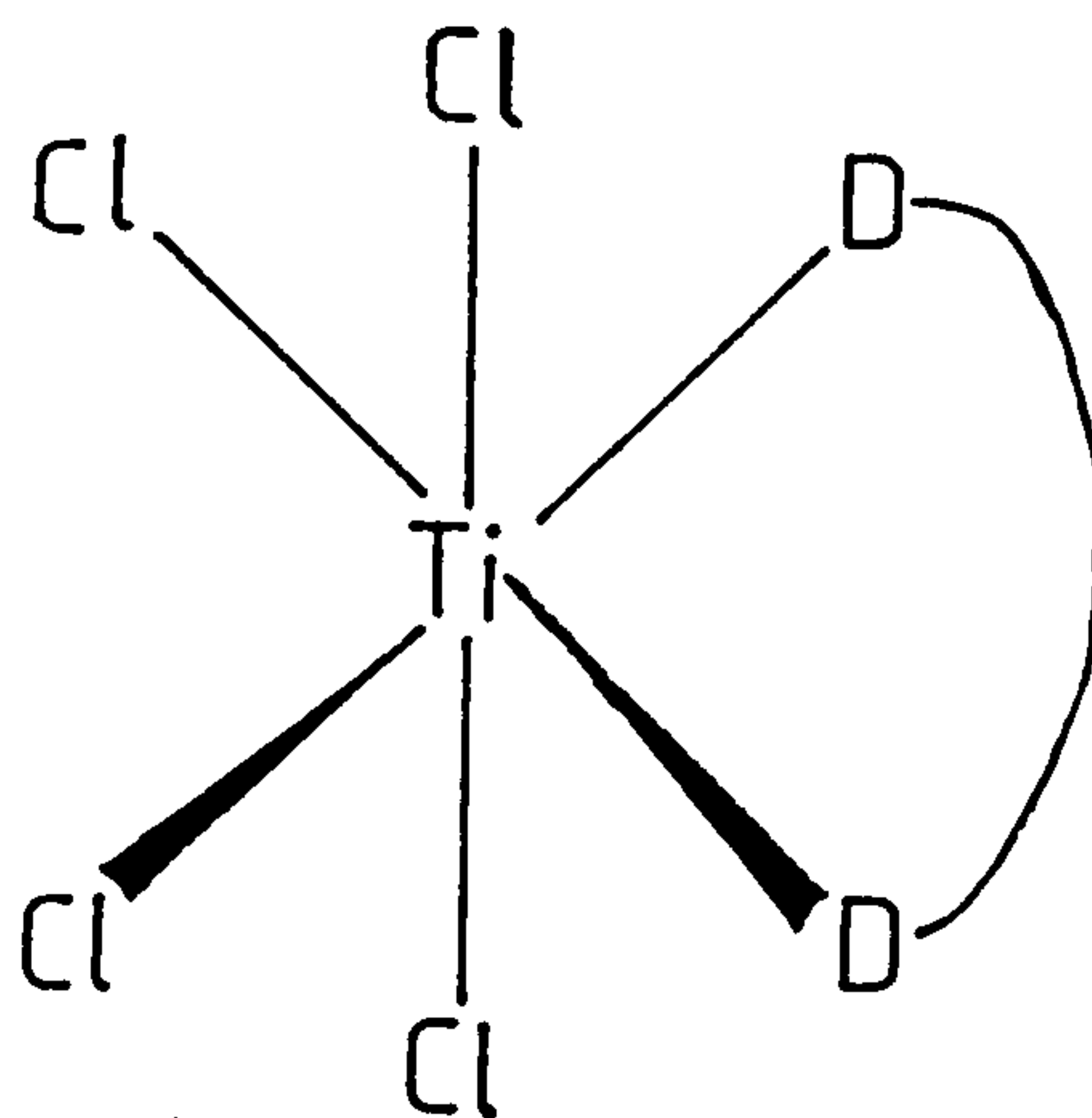
**TABLE 1.4 ADDUCTS OF TITANIUM TETRACHLORIDE OF THE TYPE  $\text{TiCl}_4 \cdot \text{L}$** 

Ligand	Donor atom	Complex	Colour	M.p/ $^{\circ}\text{C}$	Ref.
Acetophenone	O	$\text{TiCl}_4 \cdot \text{C}_6\text{H}_5\text{COCH}_3$	yellow	137-139 dec	72
Benzoyl Chloride	O	$\text{TiCl}_4 \cdot \text{C}_6\text{H}_5\text{COCl}$	yellow	63	72
Acetone	O	$\text{TiCl}_4 \cdot (\text{CH}_3)_2\text{CO}$	yellow	93-97	75
2-Butanone	O	$\text{TiCl}_4 \cdot \text{CH}_3(\text{C}_2\text{H}_5)\text{CO}$	yellow	105-110	75
Para-toluic acid	O	$\text{TiCl}_4 \cdot \text{CH}_3\text{C}_6\text{H}_4\text{COOH}$	yellow/orange	180 dec	76
Trimethylamine	N	$\text{TiCl}_4 \cdot \text{N}(\text{CH}_3)_3$	yellow	-	77
Triphenylphosphine	P	$\text{TiCl}_4 \cdot (\text{C}_6\text{H}_5)_3\text{P}$	red-violet	147.5-149	78
Triphenylarsine	As	$\text{TiCl}_4 \cdot (\text{C}_6\text{H}_5)_3\text{As}$	red-black	126-128	78

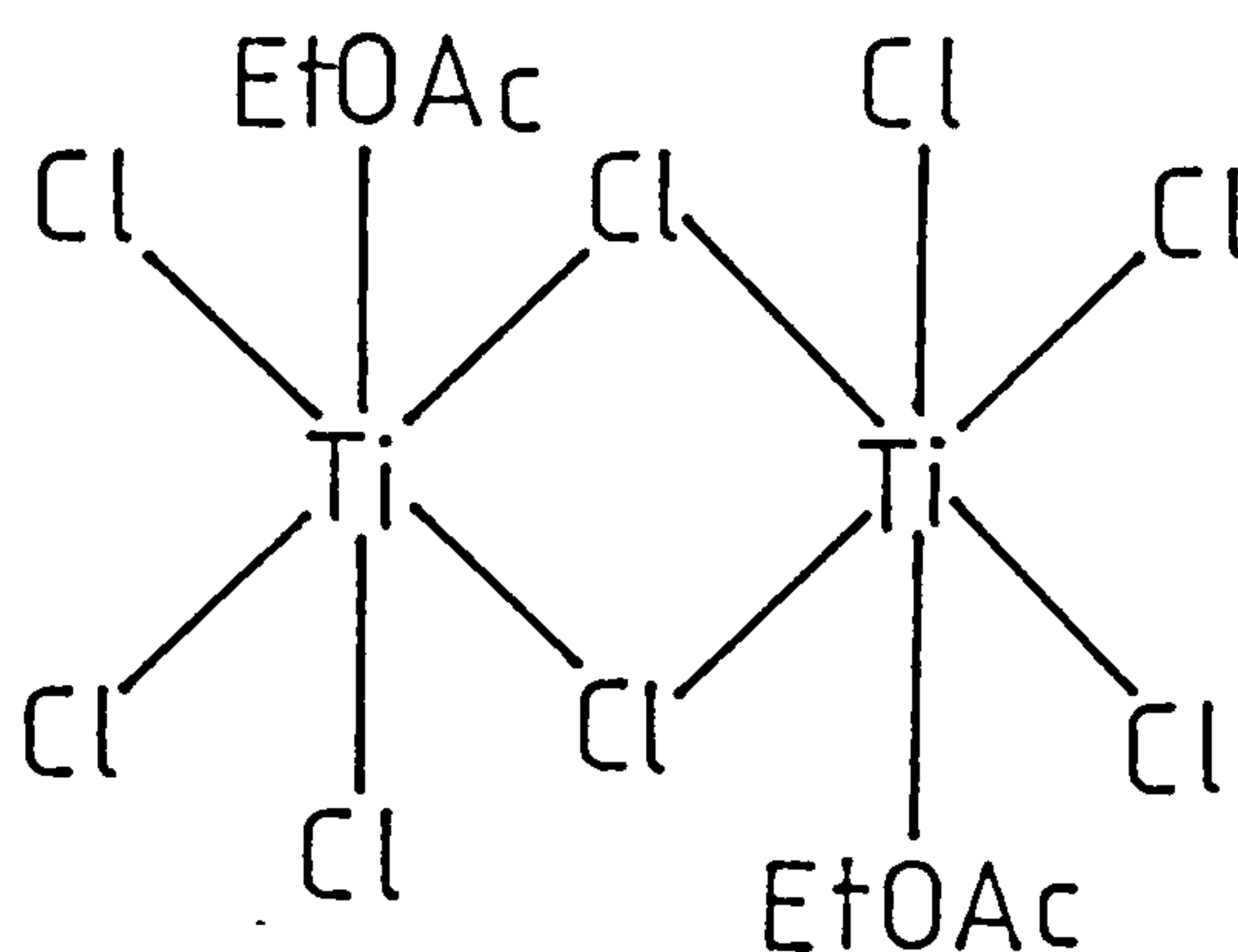
**TABLE 1.5 ADDUCTS OF TITANIUM TETRACHLORIDE WITH BIDENTATE LIGANDS**

Ligand	Donor atom	Complex	Colour	M.p/ $^{\circ}\text{C}$	Ref.
Diethyl Oxalate	O	$\text{TiCl}_4 \cdot (\text{COOC}_2\text{H}_5)_2$	yellow	104-105	79
1,2 Diphenylthioethane	S	$\text{TiCl}_4 \cdot (\text{C}_6\text{H}_5\text{SCH}_2)_2$	red	140	80
2,2 - Bipyridyl	N	$\text{TiCl}_4 \cdot \text{C}_{10}\text{H}_8\text{N}_2$	yellow	>300	64
Ethylenebis [diphenylphosphine]	P	$\text{TiCl}_4 \cdot [\text{Ph}_2\text{P}_2\text{C}_2\text{H}_4]$	red	178 dec	79





The  $\text{TiCl}_4 \cdot \text{L}$  adducts mostly attain six coordinate octahedral geometry by forming chloro-bridged dimers as illustrated by the X-ray structure of  $\text{TiCl}_4 \cdot \text{EtOAc}$ (82).



An exception to this behavior is the trimethylamine adduct  $\text{TiCl}_4 \cdot \text{N}(\text{CH}_3)_3$  which has been shown to be five coordinate(77).

Certain arsines can cause the titanium (IV) centre to become seven or eight coordinate. The triarsines methylbis(o-dimethylarsinophenyl)arsine and tris -1,1,1, - (dimethylarsinomethyl)ethane upon reaction with  $\text{TiCl}_4$  give seven coordinate complexes(83). The diarsine o-phenylenebis (dimethylarsine) upon reaction with  $\text{TiCl}_4$  gives the eight coordinate

complex  $\text{TiCl}_4 \cdot 2$  diarsine. This has a triangular dodecahedral structure(84). The reasons for this behavior with arsines are as yet unclear. Titanium also has a coordination number of eight in  $\text{Ti}(\text{NO}_3)_4$  in which the nitrate ion acts as a bidentate oxygen donor group(85).

Titanium tetrachloride forms compounds with ligands such as acetylacetone by HCl elimination. The  $\text{TiCl}_2(\text{acac})_2$  complex has a six coordinate octahedral geometry with cis chlorine atoms(86). The  $\text{TiCl}_3(\text{acac})$  complex exists as a chlorine bridged dimer in which each titanium atom is six coordinate(87). Partial hydrolysis of  $\text{TiCl}_2(\text{acac})_2$  produces the compound  $[\text{TiCl}(\text{C}_5\text{H}_7\text{O}_2)]_2\text{O} \cdot \text{CHCl}_3$ . This complex contains two  $\text{TiCl}(\text{acac})_2$  units connected by an oxygen bridge(88). The titanium atoms are octahedrally coordinated with the acetylacetonate groups cis to each other. The chloroform appears to be hydrogen bonded to the oxygens of the acetylacetonate groups.

Another type of titanium compound formed by hydrogen chloride elimination is the alkoxides. These compounds are prepared by the reaction of titanium tetrachloride and the alcohol in the presence of anhydrous ammonia.

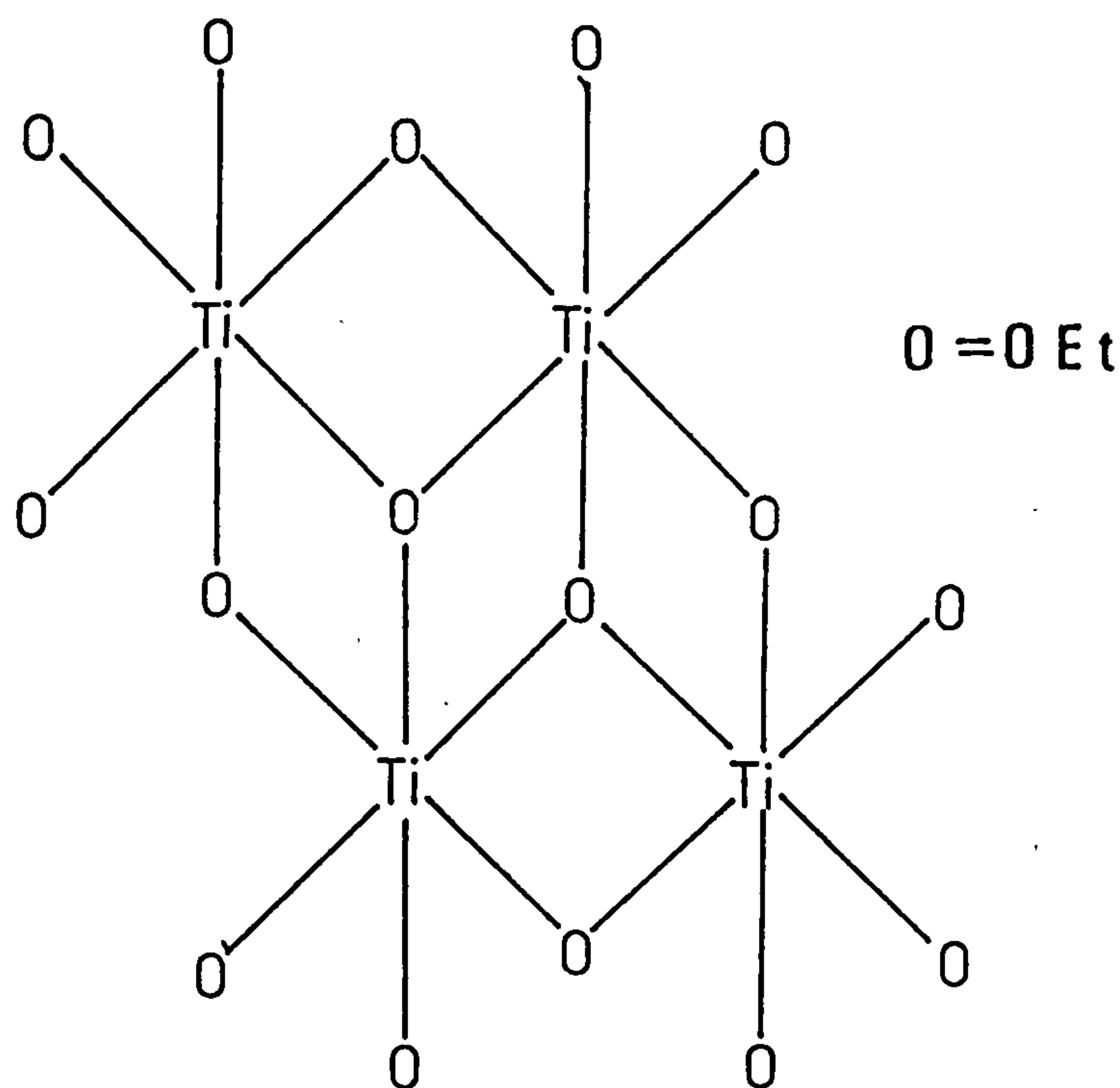


In the absence of hydrogen chloride acceptors the reaction only proceeds as far as  $\text{TiCl}_2(\text{OR})_2$ .

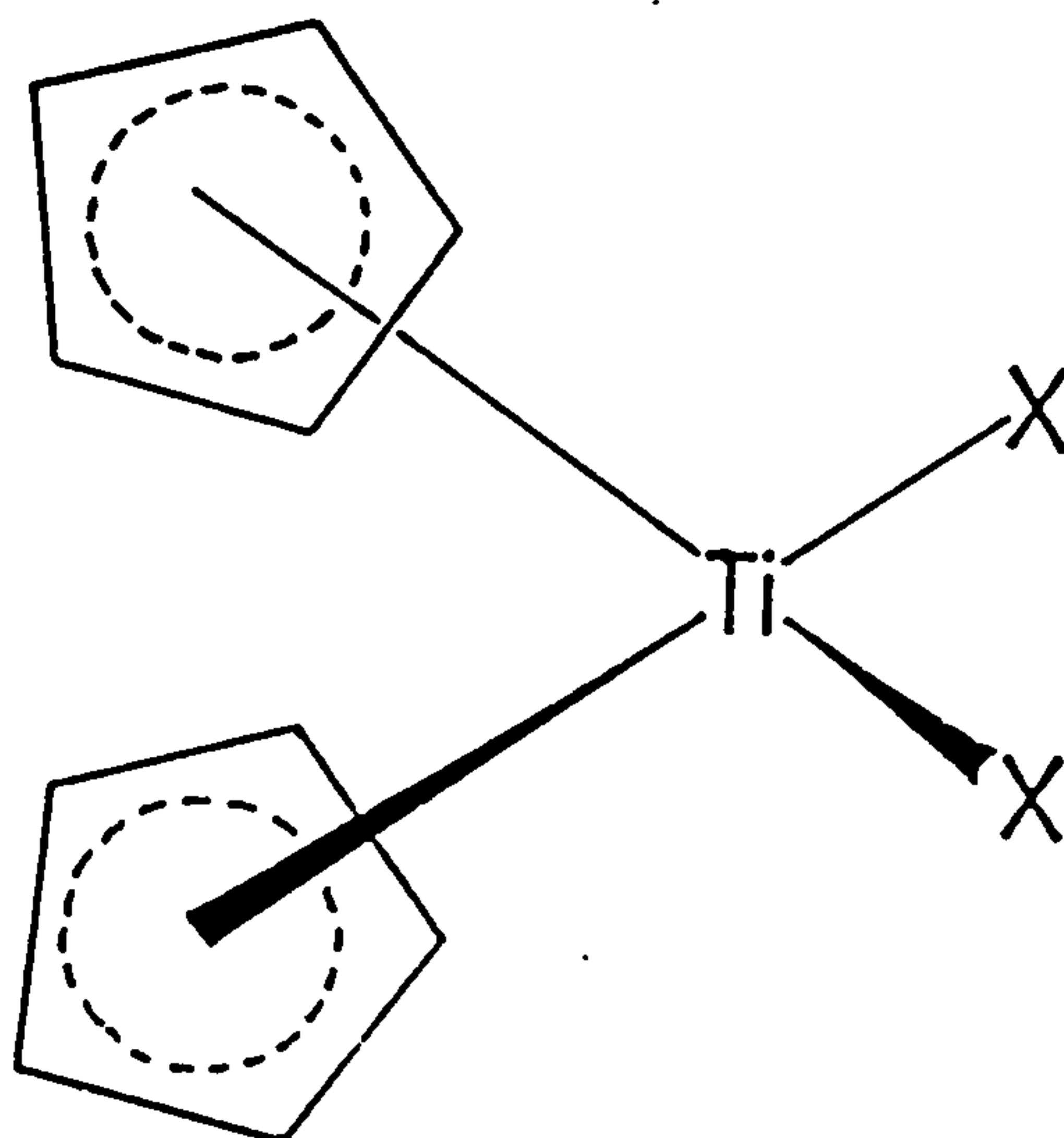
The alkoxides have a range of forms,  $\text{Ti}(\text{OMe})_4$  and  $\text{Ti}(\text{OEt})_4$  are white crystalline solids however most of the alkoxides are colourless or yellow

liquids. Most titanium alkoxides are polymeric, but those containing bulky alkoxide groups such as t-butyl are monomeric.

An X-ray study of titanium tetraethoxide has shown that the molecule is tetrameric as shown below:



Many organometallic compounds of titanium (IV) are known most of these containing the cyclopentadienyl group. Complexes of the type  $\text{TiX}_3\text{Cp}$  are prepared from the tris-alkoxide species by reaction with acetyl halide<sup>(89)</sup>. The majority of titanium organometallic compounds are bis (cyclopentadienyl) derivatives.  $\text{TiX}_2\text{Cp}_2$  is prepared by the reaction of titanium tetrachloride and a cyclopentadienyl derivative of Mg, Li or Tl. These compounds have a tetrahedral configuration as shown overleaf:



The organometallic derivatives have an extensive chemistry reacting with most ligands to give organometallic titanium complexes<sup>(89)</sup>

## TITANIUM CARBOXYLATES

### TITANIUM (III) CARBOXYLATES

#### Monocyclopentadienyltitanium (III) carboxylates

Organotitanium (III) carboxylates of formula  $\text{CpTi}(\text{O}_2\text{CR})_2$  have been prepared by a number of methods. Coutts and coworkers<sup>(90)</sup> made the carboxylates in two ways:

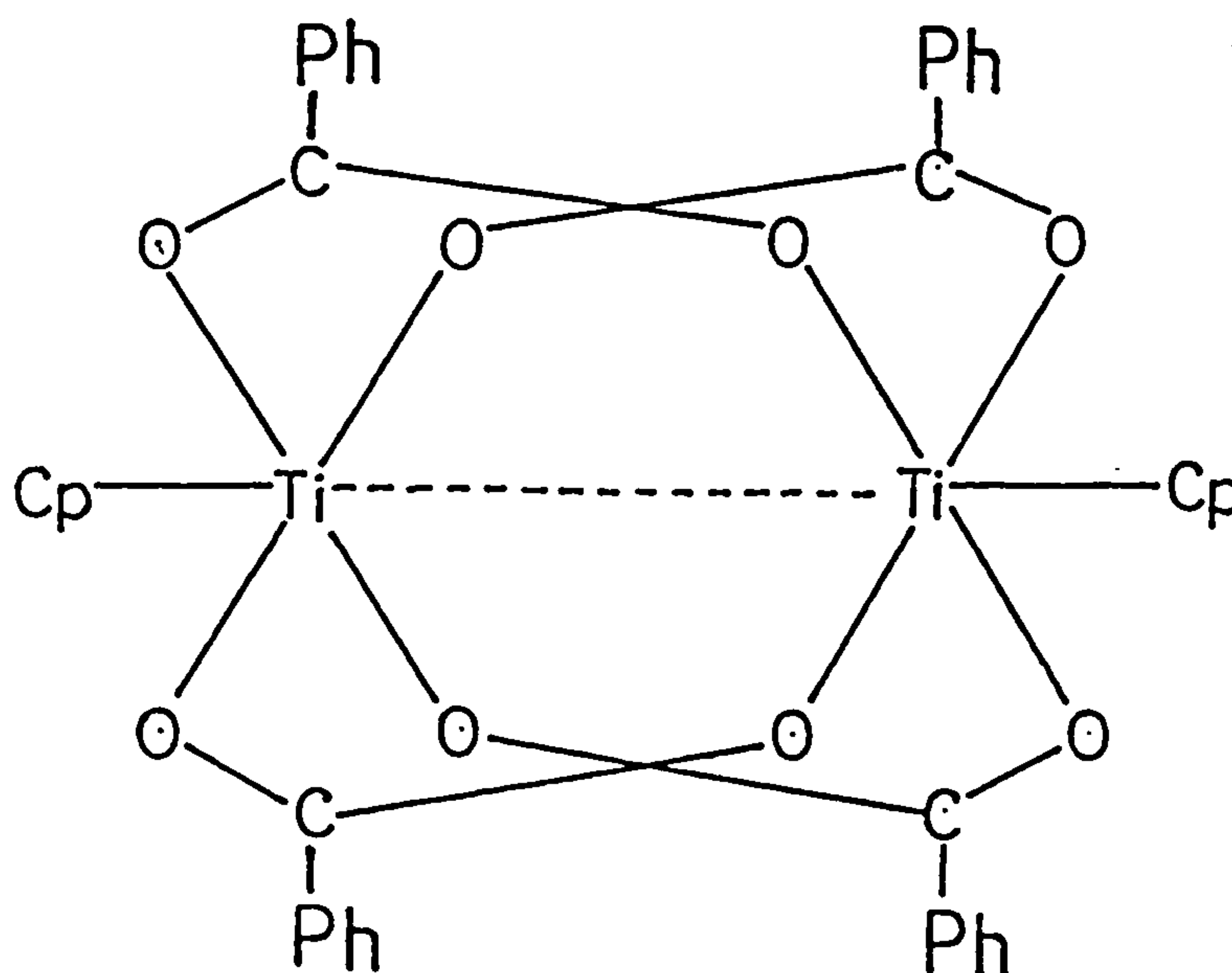
- (i) Reaction of the sodium salt of an appropriate carboxylic acid with  $\text{CpTiCl}_2$  in tetrahydrofuran. The product is purified by sublimation. The sublimation process causes the formation of some  $\text{Cp}_2\text{Ti}(\text{O}_2\text{CR})$ .



(ii) Reaction of  $\text{CpTiCl}_2$  with the carboxylic acid in the presence of an amine. This method gave the required carboxylate in 70-90% yield.

Razuvaev<sup>(91)</sup> reported that  $\text{CpTi}(\text{O}_2\text{CC}_6\text{H}_5)_2$  may be obtained by the reaction of benzoyl peroxide and  $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$ . The other products of the reaction were benzene and a polymeric ester.

Ebulliometric experiments indicate that  $\text{CpTi}(\text{O}_2\text{CR})_2$  ( $\text{R} = \text{CH}_2\text{CH}_3$  or  $\text{CH}_2\text{CH}_2\text{CH}_3$ ) is dimeric in benzene solution<sup>(90)</sup>. Infra-red data indicates the presence of bridging carboxylates. X-ray structural measurements<sup>(92)</sup> show that  $\text{CpTi}(\text{O}_2\text{CC}_6\text{H}_5)_2$  is a dimer with four bridging carboxylates.



$(\text{CpTi}(\text{O}_2\text{CC}_6\text{H}_5)_2)_2$



The carboxylates are almost diamagnetic over the temperature range 100-300K however the more soluble species are sufficiently paramagnetic to cause line broadening in the NMR spectra<sup>(90)</sup> It has been proposed that the pairs of titanium atoms are antiferromagnetically coupled through a Ti ( $d_{xy}$ ) -  $\Pi$  (carboxylate) - Ti ( $d_{xy}$ ) superexchange pathway<sup>(90)</sup>.

### Bis(cyclopentadienyl) titanium (III) carboxylates

Bis (cyclopentadienyl) titanium(III) carboxylates are generally prepared by the reaction of  $\text{Cp}_2\text{TiCl}$  and the sodium or potassium salt of an appropriate acid. Either air-free water or tetrahydrofuran may be used as solvent<sup>(93,94)</sup>. An extensive range of dicarboxylates has been prepared by the reaction between a carboxylic acid and  $\text{Cp}_2\text{Ti}(\text{CO})_2$ <sup>(97)</sup>. All the compounds are very sensitive to air; the dicarboxylato compounds spontaneously inflame. Properties of some  $\text{Cp}_2\text{Ti}(\text{O}_2\text{CR})$  complexes are shown in Table 1.6.

The structures of the pivalate and benzoate monocarboxylato species have been determined<sup>(94,37)</sup>. The compounds are monomeric with a symmetrical bidentate chelating carboxylate ligand.

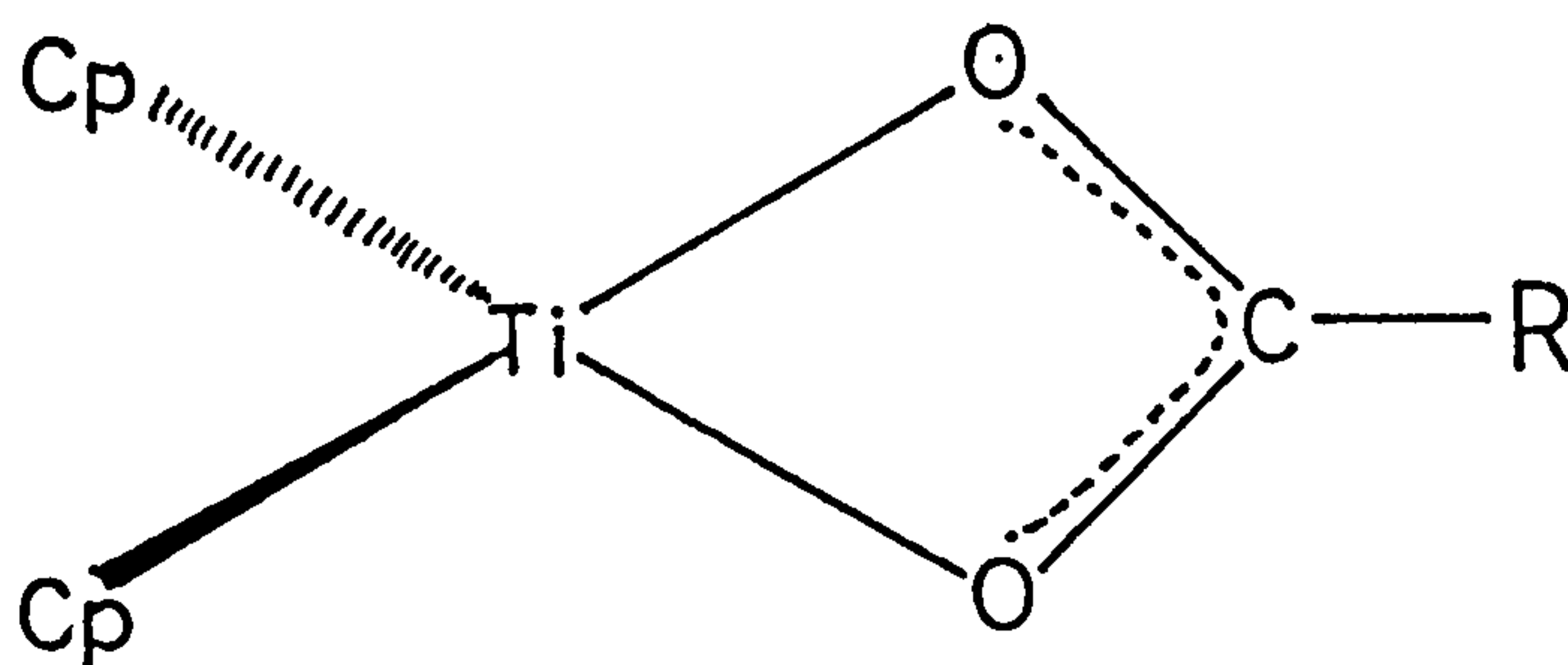


TABLE 1.6 PROPERTIES OF  $\text{Cp}_2\text{Ti}(\text{O}_2\text{CR})$  SPECIES

Compound	Colour	Melting Point °C	Reference
$\text{Cp}_2\text{Ti}(\text{O}_2\text{CH})$	Green	92	93
$\text{Cp}_2\text{Ti}(\text{O}_2\text{CCH}_3)$	Blue	110	93
$\text{Cp}_2\text{Ti}(\text{O}_2\text{C}(\text{CH}_2)_8\text{CH}_3)$	Blue	5	93
$\text{Cp}_2\text{Ti}(\text{O}_2\text{C}(\text{CH}_2)_{16}\text{CH}_3)$	Blue	35	93
$\text{Cp}_2\text{Ti}(\text{O}_2\text{CC}_6\text{H}_5)$	Dark Green	83-85	93
$[\text{Cp}_2\text{Ti}]_2(\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2)$	Grey Blue	245-250 (dec)	93
$[\text{Cp}_2\text{Ti}]_2(\text{O}_2\text{CC}_5\text{H}_6\text{CO}_2)$	Blue	-	94
$[\text{Cp}_2\text{Ti}]_2(\text{O}_2\text{CCH}=\text{CHCO}_2)$ ( <i>cis</i> )	Green	290-300 (dec)	93
$[\text{Cp}_2\text{Ti}]_2(\text{O}_2\text{CC}_4\text{H}_6\text{CO}_2)$	Blue	-	94
$[\text{Cp}_2\text{Ti}]_2(\text{O}_2\text{CCH}=\text{CHCO}_2)$ ( <i>trans</i> )	Mauve	260-262 (dec)	93

The structures of the dicarboxylato complexes  $[\text{Cp}_2\text{Ti}] (\text{O}_2\text{CC}_6\text{H}_5\text{CO}_2)$  and  $[\text{Cp}_2\text{Ti}]_2 (\text{O}_2\text{CC}_4\text{H}_6\text{CO}_2)$  have been determined<sup>(94)</sup>. The molecules are dimers with one chelating carboxylate on each titanium, the molecule being held together by the alkyl or aryl backbone of the carboxylate ligand.

The monomeric benzoate shows curious magnetic behavior. In the solid state there is an antiferromagnetic exchange interaction. It was suggested this is due to intermolecular exchanges arising from the molecular packing in the solid<sup>(94)</sup>.

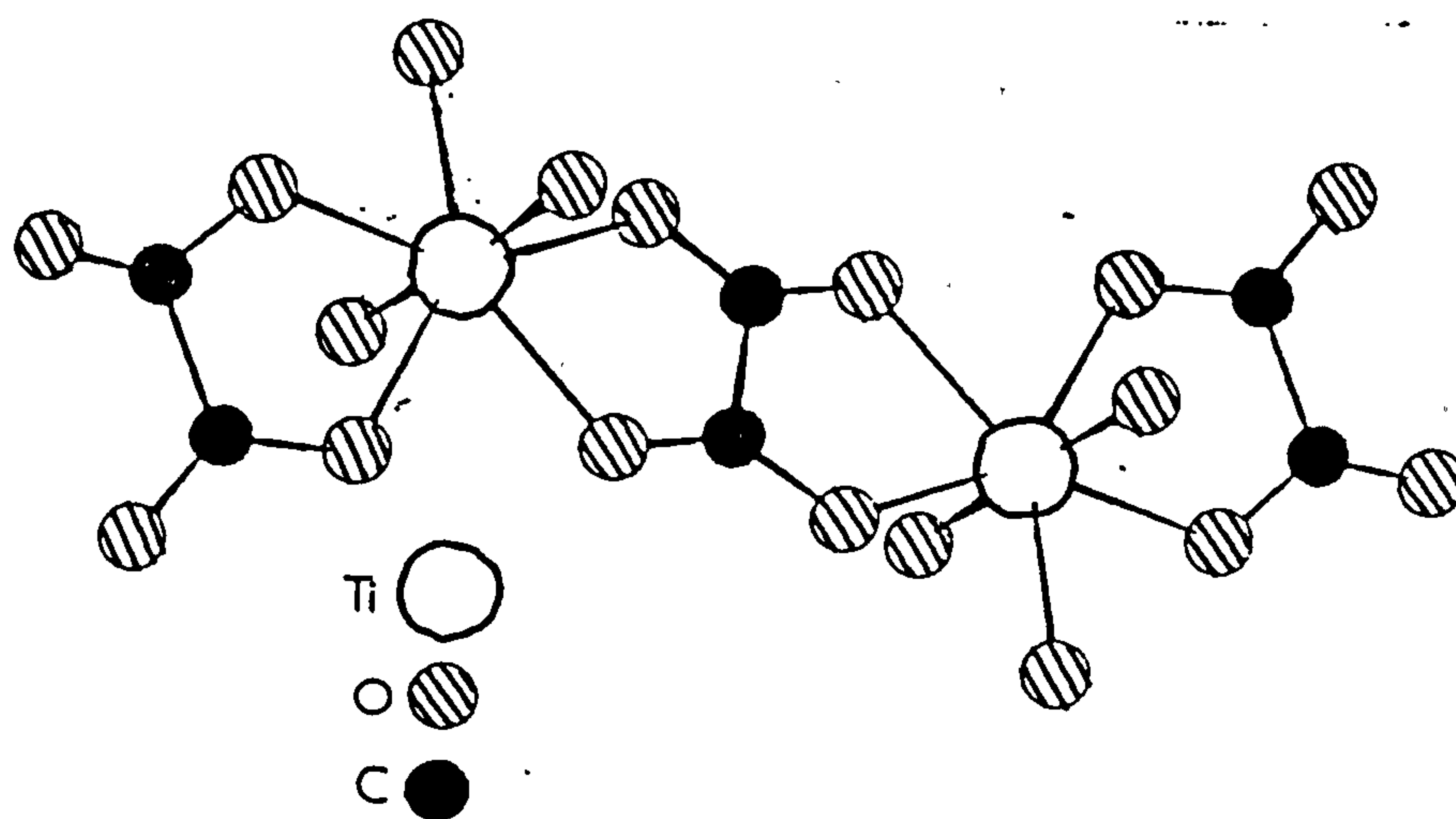
### **Titanium (III) chloro and tris-carboxylates**

Titanium (III) chloride is reported to react with acetic anhydride to give the complexes  $\text{TiCl}_2(\text{O}_2\text{CCH}_3)$  and  $\text{TiCl}(\text{O}_2\text{CCH}_3)$ <sup>(95)</sup>. The compounds are brown insoluble solids. The two compounds have different magnetic properties, the diacetate showing no field dependence and the monoacetate showing strong field dependence. It has been suggested that the acetates are bidentate bridging<sup>(95)</sup>.

Very little work has been done on titanium (III) triscarboxylates. It was reported in 1962 that  $\text{Ti}(\text{O}_2\text{CCH}_3)_3$  is formed in the reaction of formic acid with basic titanium carbonate<sup>(96)</sup>.

An unusual seven coordinate complex  $\text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  was reported by Fowles and coworkers<sup>(98)</sup>. The titanium atoms have a pentagonal bipyramidal geometry. The compound contains both chelating and bridging oxalates as well as coordinated water.

# THE STRUCTURE OF $\text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$





## TITANIUM (IV) CARBOXYLATES

### Monocyclopentadienyltitanium (IV) carboxylates

The monocyclopentadienyltitanium (IV) carboxylates of the type  $\text{CpTi}(\text{O}_2\text{CR})_3$  are generally prepared by reaction of a metal salt of a carboxylic acid with  $\text{CpTiCl}_3$ . eg.:

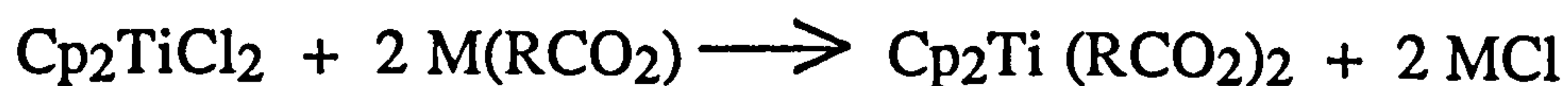


Most work on these compounds has been performed by Soviet investigators. They report that the yellow or orange solids are soluble in polar organic solvents and are more thermally sensitive than the bis(cyclopentadienyl) titanium (IV) carboxylates(33).

Little structural evidence is available, but it has been suggested from infra-red evidence that both mono and bidentate carboxylate ligands are present(99).

### Bis(cyclopentadienyl)titanium (IV) carboxylates

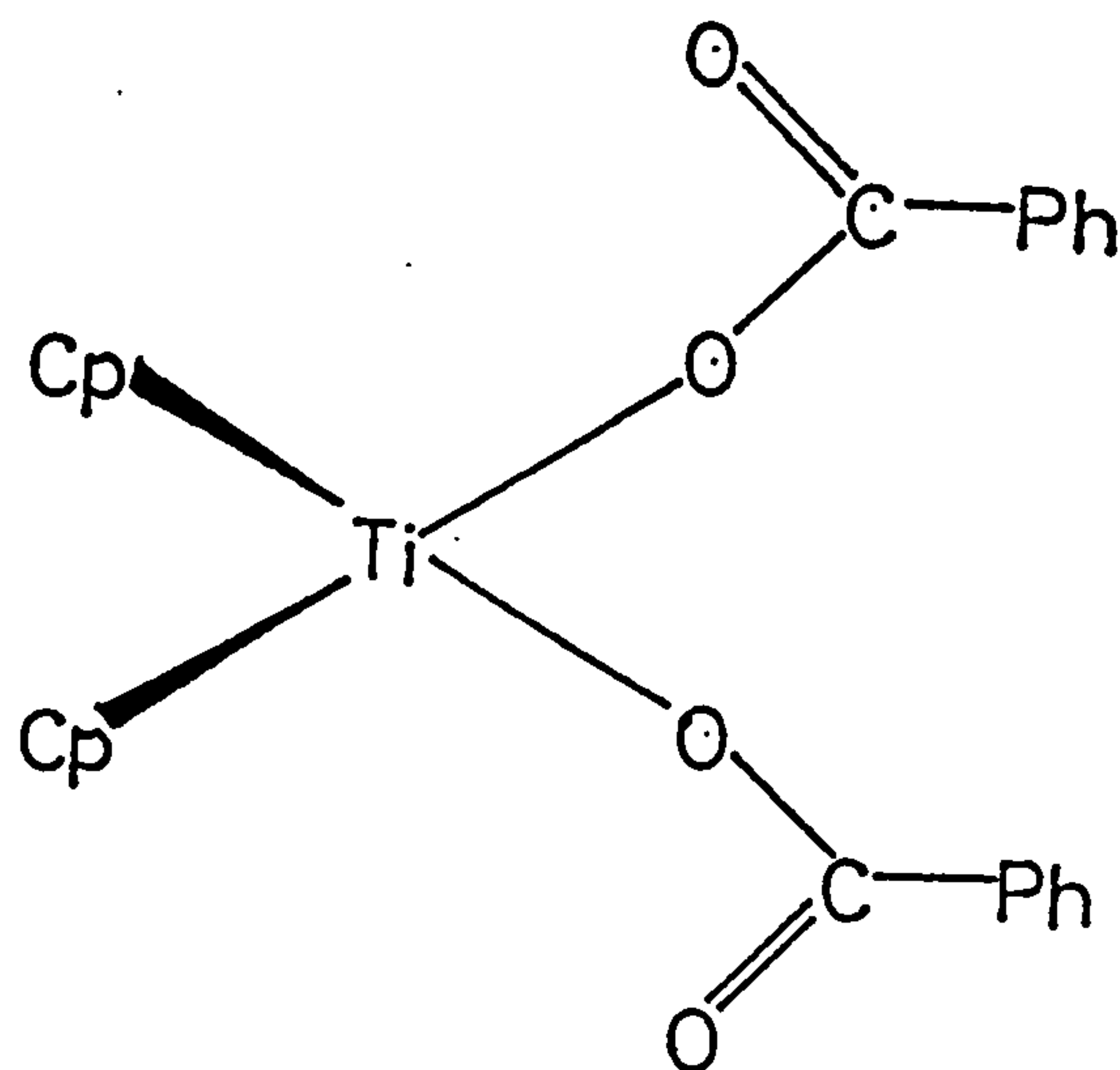
A large number of bis(cyclopentadienyl)titanium (IV) carboxylates of the type  $\text{Cp}_2\text{Ti}(\text{O}_2\text{CR})_2$  have been made. They are generally prepared by reaction of a silver or alkali metal carboxylate with  $\text{Cp}_2\text{TiCl}_2$  in an organic solvent(100-102). An alternative method is the direct reaction of  $\text{Cp}_2\text{TiCl}_2$  with the carboxylic acid in chloroform(103). eg.



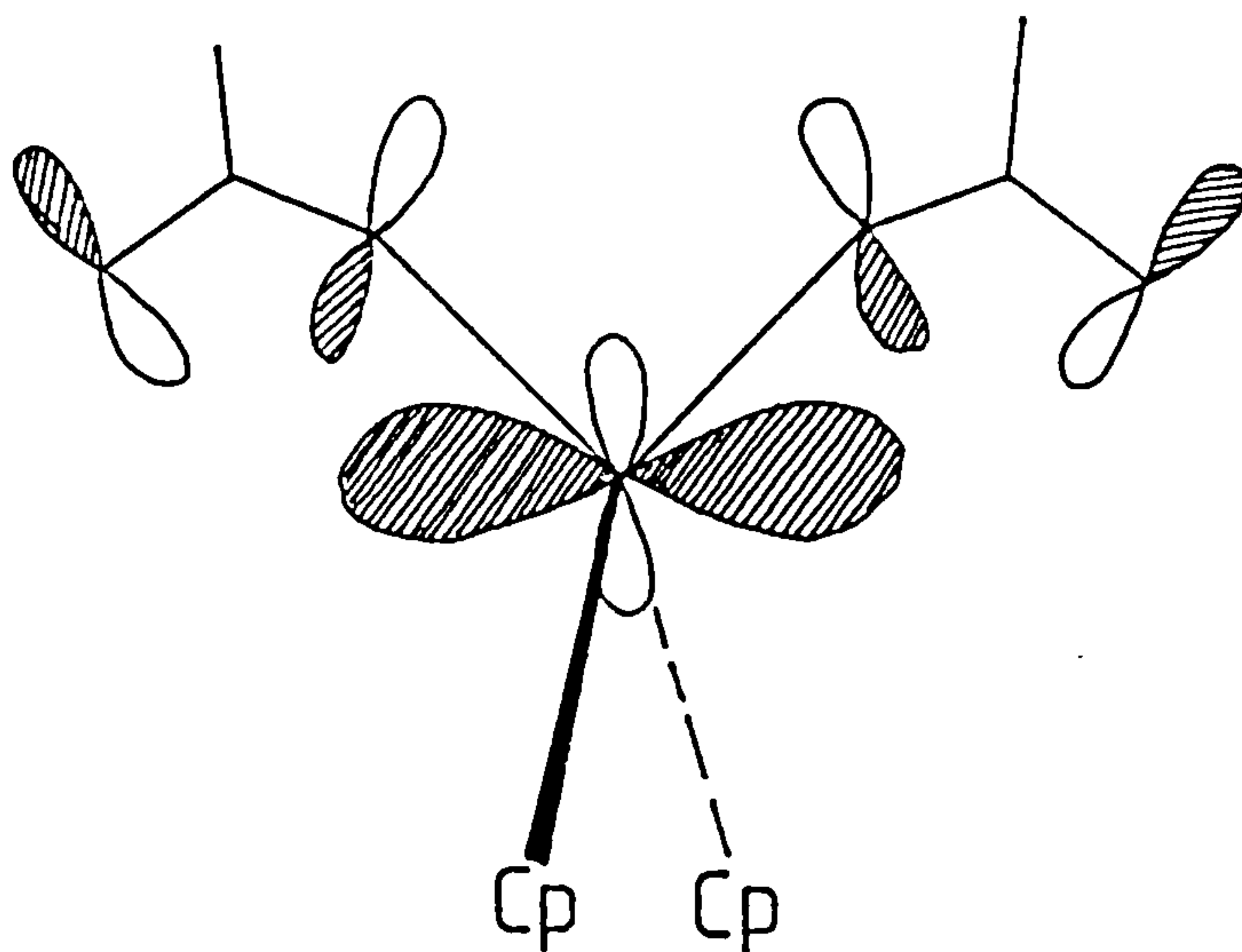
The structures of the benzoate(104,105) and p-nitrobenzoate(106) derivatives have been determined by X-ray diffraction. In both complexes the



titanium atom has a distorted tetrahedral geometry being surrounded by two cyclopentadienyl rings and two unidentate carboxylate ligands.



It has been suggested that these complexes achieve an 18 electron configuration through Ti-O  $\Pi$  bonding<sup>(104)</sup>. Molecular orbital calculations performed by Fay and coworkers show the existence of a strong  $\Pi$  interaction between the  $1a_1$  orbital of the  $(\eta^5 - C_5H_5)_2Ti^{2+}$  fragment and in-plane p orbitals of the coordinated benzoate oxygen atoms<sup>(104)</sup> This is shown in the following diagram.



The structure of a second crystalline modification of the benzoate led to the proposal that one benzoate group bonds through a normal Ti - O  $\sigma$  bond but the Ti - O bond from the other benzoate has additional  $\Pi$  - bond character<sup>(105)</sup>

Bis(methyl-cyclopentadienyl)titanium (IV) carboxylates have been prepared for a range of acids. It was suggested that for R = CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub> the carboxylate ligands are bidentate chelating and for R = CH<sub>2</sub>Cl or CHCl<sub>2</sub> the carboxylate ligands are unidentate<sup>(107)</sup> This suggestion was made on the basis of infra-red evidence and thus may be suspect.

### Titanium (IV) tetracarboxylates

Many attempts have been made to prepare Ti(O<sub>2</sub>CR)<sub>4</sub> species. Mateos claims to have made Ti(O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>(108)</sup>. No structural or chemical evidence is available for this compound.

Thiele and Panse prepared Ti(O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and Ti(O<sub>2</sub>CCH<sub>2</sub>Cl)<sub>4</sub> by the reaction of (CH<sub>3</sub>)<sub>4</sub>Ti and the appropriate acid. It was reported that the compounds contain both unidentate and bidentate carboxylate groups<sup>(109)</sup> In the reaction between (CH<sub>3</sub>)<sub>4</sub>Ti and CF<sub>3</sub>CO<sub>2</sub>H reduction occurs and the titanium (III) species Ti(O<sub>2</sub>CCF<sub>3</sub>)<sub>3</sub> is produced.

It is claimed that Ti(O<sub>2</sub>CCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> may be prepared by the sequential addition of phenylacetic acid to titanium tetrachloride<sup>(110)</sup> Miller and coworkers claim to have prepared Ti(O<sub>2</sub>CCHBr<sub>2</sub>)<sub>4</sub> by the reaction of TiCl<sub>4</sub> and dibromoacetic acid<sup>(111)</sup>

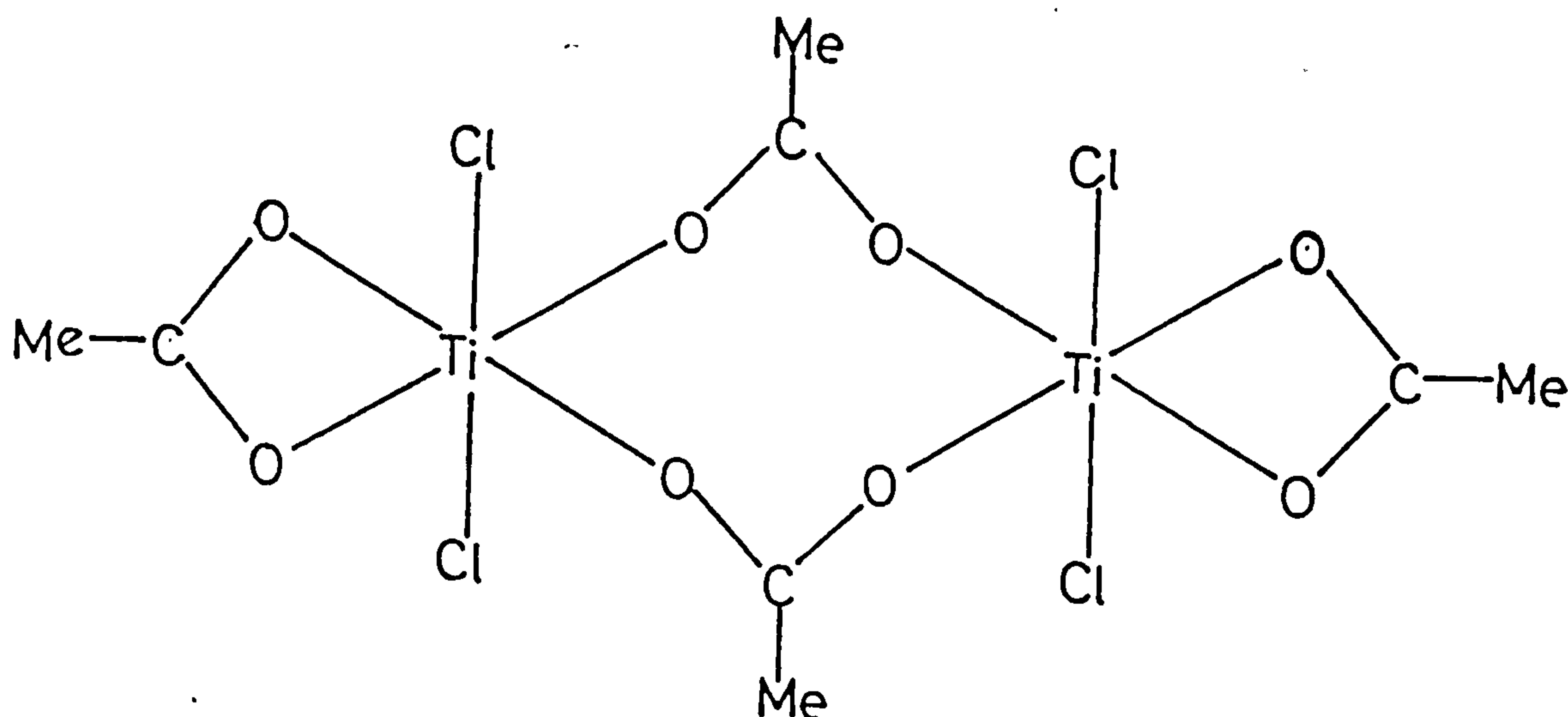
## Titanium (IV) monochlorotriscarboxylates

Jaura and coworkers claim to have prepared  $\text{TiCl}(\text{O}_2\text{CCH}_2\text{C}_6\text{H}_5)_3$  by addition of phenylacetic acid to titanium tetrachloride<sup>(110)</sup> The compound is reported to be a reddish-brown sticky mass. It was characterised by titanium and chlorine analysis.

## Titanium (IV) bishalobiscarboxylates

The bisacetate was first prepared by Reichart in 1924<sup>(112)</sup> The bishcarboxylates are generally prepared by reaction of titanium tetrahalide with a slight excess of carboxylic acid<sup>(110,112,113,114)</sup> A solvent may be used for some acids.

A wide range of  $\text{TiCl}_2(\text{RCO}_2)_2$  type compounds has been made, ( $\text{R} = (\text{CH}_3)_3\text{C}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_8, \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3, n - \text{C}_3\text{H}_7, n - \text{C}_4\text{H}_9, n - \text{C}_5\text{H}_{11}, \text{C}_6\text{H}_5$  and  $\text{C}_6\text{H}_5\text{CH}_2$ ). Amaudrut has prepared some bisbromobiscarboxylates for  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, (\text{CH}_3)_3\text{C}, \text{CH}_2\text{Cl}, \text{CH}_2\text{F}$  and  $\text{CHCl}_2$ <sup>(115)</sup>





A structure containing both chelating and bridging carboxylates was suggested based on comparison of the infra-red spectra of the dichlorides and dibromides(115,120).

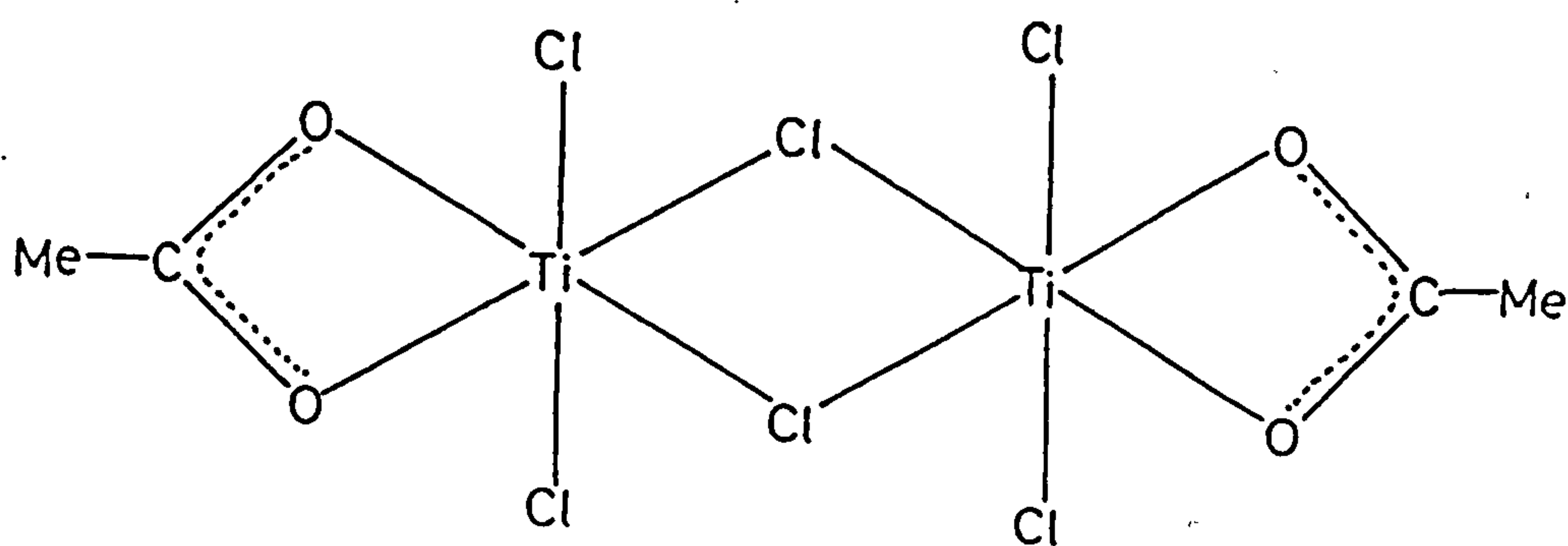
A dimeric structure with bridging carboxylates was suggested by Uh *et al* based on infra-red and NMR evidence(116).

The reactions of  $\text{TiCl}_2(\text{RCOO})_2$  species with alcohols(117),  $\text{POCl}_3$ (118) and  $\text{NOCl}$ (113) have been examined. Alcohols replace the carboxylate ligands in a two step substitution process giving  $\text{TiCl}_2(\text{OR})(\text{O}_2\text{CR})$  and  $\text{TiCl}_2(\text{OR})_2$ (117)  $\text{POCl}_3$  causes the elimination of  $\text{CH}_3\text{COCl}$  (for the diacetate) and the formation of  $\text{TiOCl}$  ( $\text{PO}_2\text{Cl}_2$ )  $\text{POCl}_3$ (118) There is no evidence for the formation of an addition complex between  $\text{TiCl}_2(\text{RCO}_2)_2$  complexes and  $\text{NOCl}$ (119)

### Titanium (IV) trischloromonocarboxylates

Titanium (IV) trischloromonocarboxylates, general formula  $\text{TiCl}_3(\text{RCO}_2)$ , are usually prepared by the reaction of a carboxylic acid with excess titanium tetrachloride(113,114,118)

The acetate is dimeric in benzene solution(121) Amaudrut claims that the acetate exists in two forms. One form changing to the other on heating to  $80^\circ\text{C}$ (121) A structure containing chelating carboxylate groups has been suggested(121)



The reactions of the monocarboxylates with NOCl<sup>(121,122)</sup>, POCl<sub>3</sub><sup>(118)</sup> and acid chlorides<sup>(123)</sup> have been investigated. POCl<sub>3</sub> causes the elimination of the acid chloride and production of TiOCl<sub>2</sub>.2POCl<sub>3</sub>. With NOCl the diacetate and the titanium tetrachloride.NOCl adduct are formed.



Acid chlorides give the addition product [TiCl<sub>3</sub>(RCO<sub>2</sub>)RCOCl]<sub>2</sub>.

### Mixed titanium (IV) alkoxide/carboxylates

Titanium (IV) alkoxide/carboxylates are made by reacting the tetraalkoxide with an appropriate amount of carboxylic acid.

Most mixed alkoxide/carboxylates are based upon the tetra-isopropoxide. Mehrotra prepared (o-OC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)Ti(OPri)<sub>2</sub>, (o-HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>Ti(OPri)<sub>2</sub> (O<sub>2</sub>CR) and (o-HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)Ti(OPri)(O<sub>2</sub>CR)<sub>2</sub> where R = C<sub>11</sub>H<sub>23</sub>, C<sub>15</sub>H<sub>31</sub> or C<sub>21</sub>H<sub>43</sub><sup>(124)</sup> On the basis of infra-red spectra it was suggested that the salicylic acids carboxylate group is bidentate and the fatty acids unidentate.

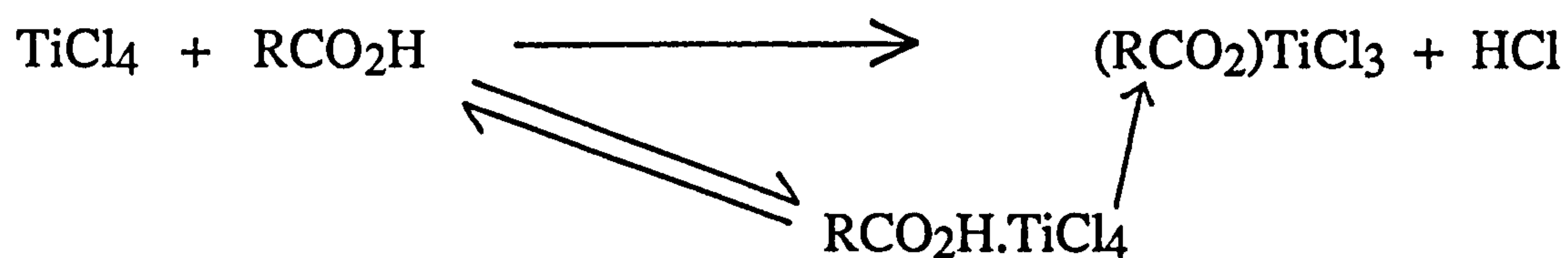
Soviet workers have made Ti(OPri)<sub>3</sub>(O<sub>2</sub>C(CH<sub>3</sub>)C=CH<sub>2</sub>) and Ti(OPri)<sub>3</sub>(O<sub>2</sub>C(CH<sub>3</sub>)C=CH<sub>2</sub>). H<sub>2</sub>C=C(CH<sub>3</sub>)CO<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>. The syntheses were performed in diethylether<sup>(125)</sup>



## Titanium tetrachloride - carboxylic acid adducts

Adducts of the type  $\text{TiCl}_4 \cdot \text{RCO}_2\text{H}$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ , 2, 4, 6 -  $(\text{CH}_3)_3\text{C}_6\text{H}_2$  and  $\text{C}_6\text{H}_5\text{CH}=\text{CH}$ ) were prepared by Susz and coworkers. Titanium tetrachloride and the acid were mixed in carbon tetrachloride<sup>(126)</sup> The acids are reported to be bonded to titanium through the carbonyl oxygen. This claim was made on the basis of the lowering of the carbonyl frequency of the acid in the infra-red spectra. No X-ray crystallographic evidence for this bonding mode was reported.

Mach and Drahorádová carried out an infra-red study on the interaction of titanium tetrachloride and carboxylic acids in solution. They found that both the complex  $\text{TiCl}_4 \cdot \text{RCO}_2\text{H}$  and the carboxylate  $\text{TiCl}_3(\text{RCO}_2)$  were formed. The proportion of each depended upon the acid strength, if a stronger acid was used the proportion of carboxylate increased. If a weaker acid was used the proportion of complex increased.<sup>(127)</sup> They produced the reaction scheme below to summarise the interaction of  $\text{TiCl}_4$  with carboxylic acids.



$\text{R} = \text{CF}_3, \text{CCl}_3, \text{CF}_2\text{H}, \text{CCl}_2\text{H}, \text{CH}_3 \text{ or } \text{C}_2\text{H}_5.$

**CHAPTER 2**

**THE PREPARATION AND REACTIONS OF**

**TITANIUM (IV) TRIS(CHLORO)MONO(CARBOXYLATE)**

**COMPLEXES**

## PREVIOUS SYNTHESSES OF TITANIUM CARBOXYLATES

A number of different methods have been used to prepare titanium (IV) carboxylate complexes. Amaudrut *et al* have obtained the monoacetate, propionate, butyrate, isobutyrate and pivalate by direct reaction of the acid and titanium tetrachloride. After a violent reaction the yellow products were washed with carbon tetrachloride and petroleum ether.<sup>(113,121)</sup> The analyses of titanium and chlorine for the pivalate are high compared with the calculated values indicating the probable presence of unreacted titanium tetrachloride. This may not be surprising since in the present work we have also observed that any excess  $\text{TiCl}_4$  present in reaction products is held tenaciously even after extensive washing.

Kapoor and coworkers claim to have prepared a number of titanium (IV) monocarboxylates by reaction of excess titanium tetrachloride with a carboxylic acid in dichloromethane or carbon tetrachloride.<sup>(114)</sup> The reactants were cooled before addition of the titanium tetrachloride in order to obtain a smooth reaction. The products,  $\text{TiCl}_3(\text{RCO}_2)$   $\text{R}=\text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$  and  $\text{C}_5\text{H}_{11}$ , were characterised by elemental analyses and infra-red spectra. The analysis for the acetate is accurate however the analyses for the other complexes vary slightly from the calculated values. The acetate is reported to be insoluble in non-polar organic solvents which agrees with results previously obtained.<sup>(121,128)</sup> It appears that Kapoor and coworkers have prepared the monoacetate but the data for the other complexes do not completely justify claims for their preparation.

It is claimed that  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2)$  may be prepared by addition of a diethylether solution of phenylacetic acid to titanium tetrachloride at

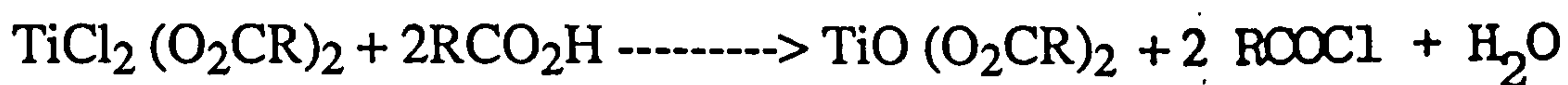
0 °C<sup>(110)</sup> The resulting yellowish brown sticky mass was only characterised by titanium and chlorine analyses. This claim for the preparation of  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2)$  must be regarded with scepticism as the reported product is inhomogenous and no spectral evidence for its formation is offered.

Amaudrut reported that the biscarboxylates may be prepared by reaction of titanium tetrachloride with an excess of carboxylic acid at 0 °C.<sup>(120)</sup> This reaction pathway has recently been investigated by D. Brown. The more recent work indicates biscarboxylates are not formed by reaction of titanium tetrachloride with excess carboxylic acid<sup>(129)</sup> An alternative method of preparation used by Kapoor and coworkers is the combination of titanium tetrachloride and excess carboxylic acid in an organic solvent such as carbon tetrachloride or dichloromethane<sup>(114)</sup>.

Reasonable elemental analyses were obtained for the products of this reaction. The infra-red spectra contained three bands due to carboxylate stretches which agrees with reports by other authors<sup>(120)</sup> However the infra-red spectra reported for the biscarboxylates are very similar to those reported for the monocarboxylates.

A recent paper reports that reaction of chlorosubstituted carboxylic acids with titanium tetrachloride produces only biscarboxylates even when the titanium tetrachloride is present in excess. Refluxing the reaction mixture in an attempt to prepare tris or tetracarboxylates gives the oxo derivative according to the equation below<sup>(114)</sup>.





This reaction scheme has some similarities to that proposed by Sartori for the interaction of titanium tetrachloride and excess trifluoroacetic acid<sup>(130)</sup>



No explanation was offered for this behavior.

Swartz and coworkers reported the preparation of the bisacetate and bispropionate by reaction of excess carboxylic acid and titanium tetrachloride followed by stirring and standing at  $-10^\circ\text{C}$  for 12 hours<sup>(131)</sup>

Few analytical details were described.

It was claimed that the bisformate can be made by the reaction of titanium tetrachloride and formic acid at  $-78^\circ\text{C}$ <sup>(132)</sup> It appears more likely that the complex  $\text{TiCl}_4 \cdot n(\text{HCO}_2\text{H})$  would be formed at such low temperatures. The same workers found that at higher temperature, hydrolysed products,  $\text{TiCl}_2 (\text{OH}) (\text{O}_2\text{CH})$  and  $\text{Ti}(\text{OH})_2 (\text{O}_2\text{CH})_2$  are obtained<sup>(132)</sup> This may be due to the presence of water in the reaction mixture. Attempts to prepare the bisformate using sodium formate also gave hydrolysed products<sup>(132)</sup>

There are no reliable reports of the synthesis of titanium (IV) triscarboxylates.



Many reports of the preparation of titanium (IV) tetracarboxylates have been published however some of these reports are over optimistic in their claims.

Jaura et al claim to have made the tetra(phenylacetate) by reaction of titanium tetrachloride with excess carboxylic acid dissolved in diethyl ether. The reaction mixture was then heated for several hours.<sup>(110)</sup> This claim was made on the basis of one inaccurate titanium analysis so may be dismissed.

The tetra(acetate) was made by reaction of  $(\text{CH}_3)_4\text{Ti}$  with acetic acid. When  $(\text{CH}_3)_4\text{Ti}$  was reacted with halide-substituted-carboxylic acids some reduction to titanium (III) occurs.<sup>(109)</sup> The products were characterised by elemental analyses, magnetic moments and infra-red spectra.

Gayer and coworkers prepared  $\text{Ti}(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{CH}_3\text{CO}_2\text{H}$  by reaction of titanium tetrachloride, acetic acid and potassium acetate in ether. The product is a crystalline yellow solid.<sup>(133)</sup>

Malhotra and coworkers reported the preparation of  $\text{Ti}(\text{CHCl}_2\text{CO}_2)_4$  and  $\text{Ti}(\text{CH}_2\text{ClCO}_2)_4$  by refluxing titanium tetrachloride with an excess of the halocarboxylic acid.<sup>(134,135)</sup> Kapoor claims that refluxing titanium tetrachloride with an excess of  $\text{CHCl}_2\text{CO}_2\text{H}$  or  $\text{CH}_2\text{ClCO}_2\text{H}$  produces only  $\text{OTi}(\text{O}_2\text{CR})_2$  type derivatives.<sup>(114)</sup> This reaction clearly requires re-investigation.

## REACTIONS OF TITANIUM (IV) CARBOXYLATES

The reactions of titanium (IV) carboxylates with a limited range of ligands have been studied previously.

The reaction of the mono and biscarboxylates with  $\text{POCl}_3$  was investigated by Amaudrut and coworkers. The monocarboxylate gave  $\text{TiOCl}_2 \cdot 2\text{POCl}_3$  and the acid chloride.<sup>(136)</sup> The products were identified by their infra-red spectra and elemental analyses.

Reaction of the biscarboxylates with  $\text{POCl}_3$  produced  $[\text{TiCl}_3(\text{PO}_2\text{Cl}_2)\text{POCl}_3]_2$ , this compound was characterised by X-ray powder photographs, infra-red spectra and elemental analysis<sup>(118)</sup>

Viard and Devin treated the monoacetate with  $\text{CH}_3\text{COCl}$  to form the addition product  $[\text{TiCl}_3(\text{CH}_3\text{CO}_2) \cdot \text{CH}_3\text{COCl}]_2$ <sup>(123)</sup>

Nitrosyl chloride ( $\text{NOCl}$ ) reacts with titanium monocarboxylates to give addition compounds of the formulation  $\text{TiCl}_3(\text{RCO}_2) \cdot \text{NOCl}$ . The biscarboxylates do not react with  $\text{NOCl}$ <sup>(113,119)</sup>

The reactions of titanium carboxylates with tertiary nitrogen bases have been studied. Kapoor and co-workers claim that both mono and biscarboxylates form 1:1 and 1:2 complexes with pyridine. Whether the 1:1 or 1:2 adduct is formed depends upon the size of the carboxylate alkyl group; when  $\text{R} = \text{CH}_3$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{CHCl}_2$  and  $\text{CCl}_3$  the 1:2 adduct is formed however if  $\text{R} = \text{C}_2\text{H}_5$ ,  $n - \text{C}_3\text{H}_7$ ,  $n - \text{C}_4\text{H}_9$  or  $n - \text{C}_5\text{H}_{11}$  the 1:1 adduct is formed.<sup>(114)</sup> In a separate report Kapoor claims that  $\text{TiCl}_2(\text{O}_2\text{CH})_2$  forms 1:2 addition compounds with pyridine,  $\gamma$  - picoline and quinoline<sup>(132)</sup> As the

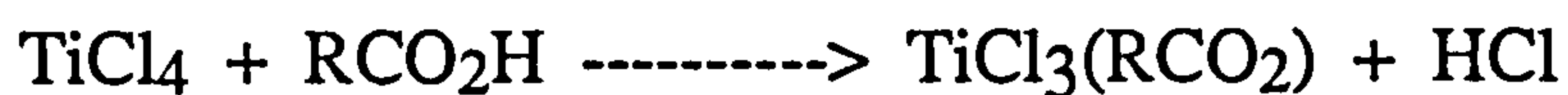
original preparation of the bisformate is suspect the formation of the adduct appears unlikely.

Malhotra and co-workers investigated the reaction of the tetracarboxylates  $\text{Ti}(\text{CHCl}_2\text{CO}_2)_4$  and  $\text{Ti}(\text{CH}_2\text{ClCO}_2)_4$  with pyridine. In both cases it was claimed that the addition compound  $\text{Ti}(\text{RCO}_2)_4 \cdot 2\text{py}$  was formed<sup>(134,135)</sup> Again as the original preparation of the tetracarboxylate is disputed the formation of the adduct must be regarded as unproven.

## I. GENERAL PREPARATIVE METHODS FOR TITANIUM (IV) MONOCARBOXYLATES

There are three main methods for making  $\text{TiCl}_3(\text{RCO}_2)$  species, these are:

- (i) Direct reaction of titanium tetrachloride and the carboxylic acid. This method has the advantage that no solvent is used so the products are easily collected. The disadvantages of this method are that it is difficult to control the rate of the reaction, and the excess titanium tetrachloride is difficult to remove from the final product.



- (ii) Reaction of titanium tetrachloride and carboxylic acid in an organic solvent. This method has the advantages that the reaction may be conveniently controlled by varying the concentrations of reactants and the products can be easily washed free of any titanium tetrachloride. However if the product is very soluble in the solvent it may be difficult to isolate.



(iii) Reaction of a metal carboxylate with titanium tetrachloride.



Many metal carboxylates react with titanium tetrachloride to form titanium carboxylates. The carboxylates used are usually those of the alkali and alkaline earth metals although silver carboxylates have been utilised. The metal halide is formed and can generally be filtered off leaving the soluble titanium carboxylates.

In order to dissolve the metal carboxylate a polar solvent such as diethyl ether or ethyl acetate must be used<sup>(33)</sup>. These solvents form adducts with titanium tetrachloride thus complicating the reaction. In the present work it has been found that the metal halide can be difficult to separate particularly if the precipitate is colloidal.

In our work we have mainly used preparative method (ii). In general this method works well. Some carboxylates were made using metal carboxylates when reaction of  $\text{TiCl}_4$  and  $\text{RCO}_2\text{H}$  in a solvent did not give the required product.

The choice of solvent is very important. In many solvents the titanium carboxylates are extremely soluble which makes it difficult to isolate them in a pure form. Polar solvents such as tetrahydrofuran or ethyl acetate react with titanium (IV) compounds so cannot be used in the preparation of  $\text{TiCl}_3(\text{RCO}_2)$  species.

## II. PREPARATION OF TITANIUM (IV) TRIS(CHLORO)MONO(CARBOXYLATES)

### Preparation of $\text{TiCl}_3 (\text{C}_6\text{H}_5\text{CO}_2)$

Benzoic acid is a white crystalline solid which is soluble in many organic solvents. Its  $\text{pK}_a$  is 4.2 at  $25^\circ\text{C}$ .

The benzoate was made by the method previously described by Gordon(128). Excess titanium tetrachloride was added to a toluene solution of benzoic acid. The solution was heated for one hour and then cooled to precipitate the orange benzoate. The supernatant liquid was removed and the product washed with petroleum ether (b.p  $60-80^\circ\text{C}$ ). It was then dried *in vacuo*.

The infra-red spectrum of  $\text{TiCl}_3 (\text{C}_6\text{H}_5\text{CO}_2)$  contains bands at  $1600\text{cm}^{-1}$ ,  $1555\text{cm}^{-1}$  and  $1410\text{cm}^{-1}$  in the carboxyl stretching region. The bands at  $1600\text{cm}^{-1}$  and  $1500\text{cm}^{-1}$  may be assigned to phenyl ring vibrations. The bands at  $1555\text{cm}^{-1}$  and  $1410\text{cm}^{-1}$  are assigned to  $\nu(\text{CO}_2^-)_{\text{asym}}$  and  $\nu(\text{CO}_2^-)_{\text{sym}}$  vibrations respectively. The  $\Delta$  value, as described in chapter 1, is  $145\text{cm}^{-1}$ . Comparison with the acetates indicates this value is consistent with the presence of bridging and or chelating carboxylate groups(57).

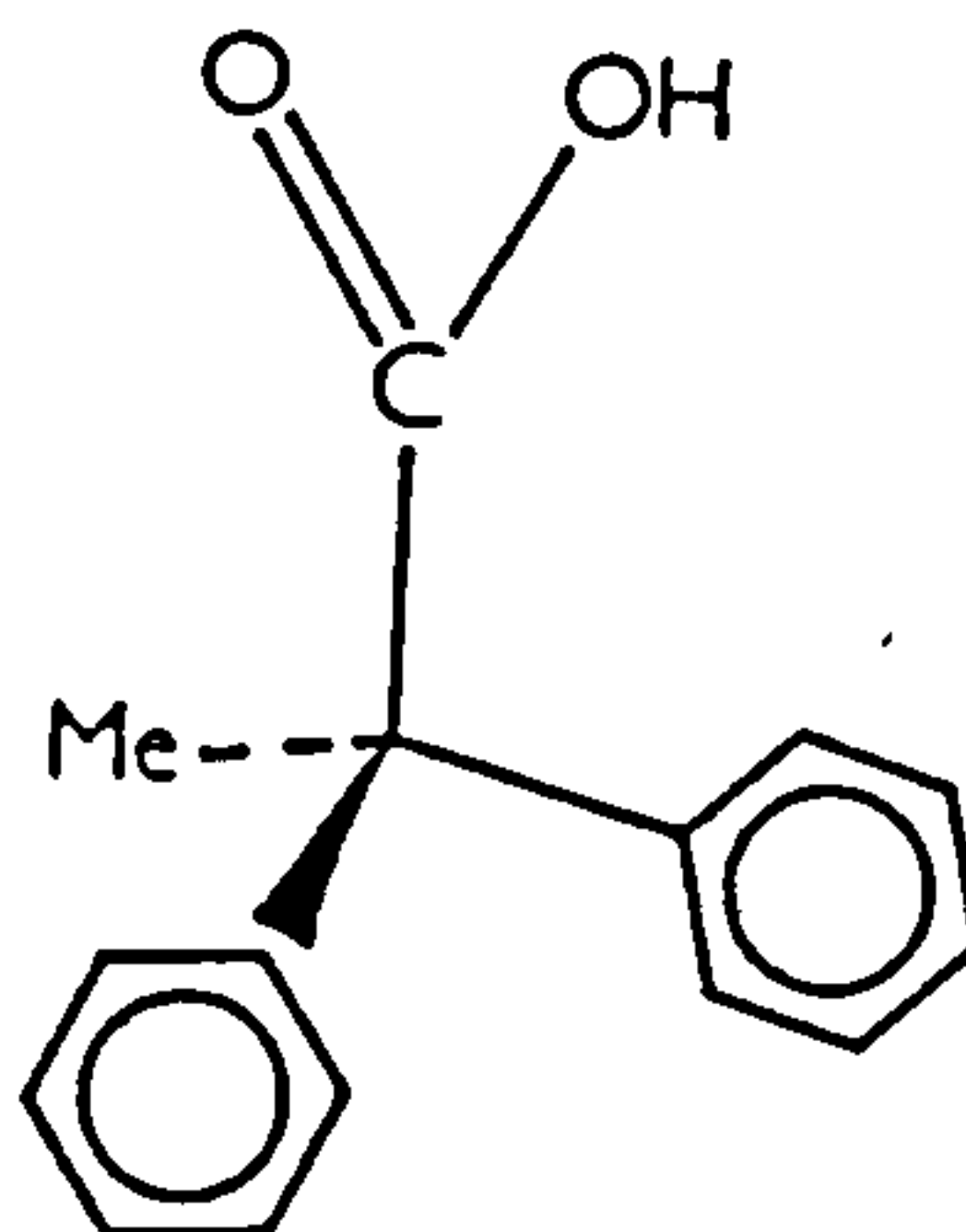
Bands at  $410\text{cm}^{-1}$ ,  $375\text{cm}^{-1}$ ,  $320\text{cm}^{-1}$ ,  $290\text{cm}^{-1}$  and  $260\text{cm}^{-1}$  are tentatively assigned to Ti-Cl vibrations. It is likely that these bands contain contributions from other infra-red active bands. Metal halide bridges are reported to give infra-red bands around  $200\text{cm}^{-1}$ , often less than  $200\text{cm}^{-1}$  (56) so the band at  $260\text{cm}^{-1}$  may be due to a titanium-chlorine-titanium bridge.

The  $^1\text{H}$  NMR spectrum of  $\text{TiCl}_3 (\text{C}_6\text{H}_5\text{CO}_2)$  has resonances at 7.5 - 8.5p.p.m. due to the phenyl protons of the carboxylate ligand.



## PREPARATION OF $\text{TiCl}_3[(\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{CCO}_2]$

2,2-Diphenylpropanoic acid is a white powder which melts at  $178^\circ\text{C}$ . Its  $\text{pK}_a$  is 5.77 at  $25^\circ\text{C}$ . Before use the acid was recrystallised from dichloromethane. The structure of 2,2 - diphenylpropanoic acid is shown below:



The compound was prepared by reaction of excess titanium tetrachloride with the 2,2 - diphenylpropanoic acid in an organic solvent. A number of solvents were tried, these included benzene, ethyl acetate, 60-80 petroleum ether, dichloromethane and diethyl ether. The best products were obtained from benzene solution and these products were extremely soluble in  $\text{CH}_2\text{Cl}_2$ , ethyl acetate, and diethyl ether. When the reaction was attempted in 60-80 petroleum ether an inhomogenous product containing black particles was obtained.

To obtain a solid product from the red benzene solution the solution was pumped to dryness giving an orange solid. The solid was then washed with petroleum ether (b.p.  $60-80^\circ\text{C}$ ) and dried *in vacuo* at room temperature.

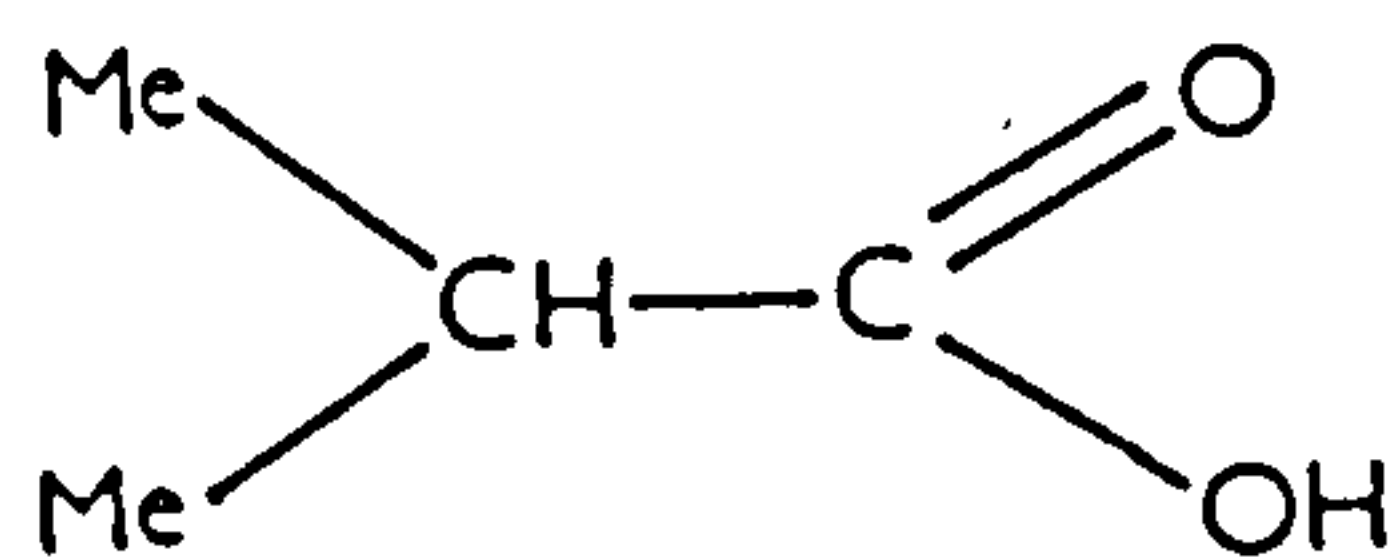
The  $^1\text{H}$  NMR spectrum of the orange product contains two resonances; a broad resonance at 7.0 - 7.4 p.p.m. due to the phenyl ring protons, and a singlet at 1.74 p.p.m. due to the methyl group of the carboxylate ligand.

The spectrum also showed some traces of weakly bound solvent which proved impossible to remove. The product contains ca. 1 solvent per 10 carboxylate groups.

The infra-red spectrum of the solid shows four bands in the carbonyl stretching region. These are at  $1645\text{cm}^{-1}$ ,  $1600\text{cm}^{-1}$ ,  $1530\text{cm}^{-1}$  and  $1490\text{cm}^{-1}$ . The bands at  $1600\text{cm}^{-1}$  and  $1490\text{cm}^{-1}$  may be assigned as phenol ring vibrations. The band at  $1645\text{cm}^{-1}$  is assigned as  $\nu(\text{CO}_2^-)_{\text{asym}}$  and the band at  $1530\text{cm}^{-1}$  as  $\nu(\text{CO}_2^-)_{\text{sym}}$ . The resulting  $\Delta$  value is  $115\text{cm}^{-1}$ . According to the criteria of Deacon and Phillips this indicates the presence of bridging and/or chelating carboxylate groups(57). Bands at  $420\text{cm}^{-1}$ ,  $385\text{cm}^{-1}$  and  $330\text{cm}^{-1}$  are assigned to Ti-Cl vibrations as they appear in the region in which such bands would be expected(56).

## PREPARATION OF $\text{TiCl}_3[(\text{CH}_3)_2\text{CHCO}_2]$

Isobutyric acid (2-methylpropanoic acid) is a colourless liquid (b.p.  $153.2^\circ\text{C}$ ) at room temperature. Its  $\text{pK}_a$  is 4.79. Before use the acid was dried using  $\text{P}_2\text{O}_5$ .



The isobutyrate was prepared by reaction of excess titanium tetrachloride with a carbon tetrachloride solution of isobutyric acid. The initial yellow solution was stirred for 12 hours and pumped to dryness. The yellow solid formed was recrystallised from  $\text{CCl}_4$ .

The  $^1\text{H}$  NMR spectrum of the product contains two resonances, a multiplet centred at 2.23 p.p.m. due to the CH proton and multiple peaks around 0.8 - 1.2 p.p.m. due to the methyl groups. In isobutyric acid the two methyl groups are equivalent and produce a singlet in the  $^1\text{H}$  NMR spectrum. The multiple peaks found in the  $^1\text{H}$  NMR spectrum of  $\text{TiCl}_3[(\text{CH}_3)_2\text{CHCO}_2]$  imply either the existence of several species in solution or inequivalence of the carboxylate ligands methyl groups. The methyl groups should be relatively far away from the metal centres and other species so it appears several slightly different forms of  $\text{TiCl}_3[(\text{CH}_3)_2\text{CHCO}_2]$  exist in the solution. A similar effect occurs in the  $^1\text{H}$  NMR spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  and is discussed in chapter 3.

The infra-red spectrum of the yellow solid has three bands in the carboxyl stretching region. These are at  $1650\text{cm}^{-1}$ ,  $1600\text{cm}^{-1}$  and  $1500\text{cm}^{-1}$ . The band at  $1650\text{cm}^{-1}$  is assigned as  $\nu(\text{CO}_2^-)_{\text{asym}}$  and the band at  $1500\text{cm}^{-1}$  as  $\nu(\text{CO}_2^-)_{\text{sym}}$ . The band at  $1600\text{cm}^{-1}$  may well contain contributions from both  $\text{CO}_2^-$  vibrations and methyl deformations. The  $\Delta$  value is  $150\text{cm}^{-1}$  which according to the Deacon and Phillips criteria is consistent with the presence of bridging and/or chelating carboxylate groups(57). Bands at  $390\text{cm}^{-1}$  and  $320\text{cm}^{-1}$  are assigned to Ti-Cl vibrations.



## ATTEMPTED PREPARATION OF $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2)$

Phenylacetic acid is a white solid which melts at 77-78.5 °C. Its  $\text{pK}_a$  is 4.5 (in 10% EtOH aq.). Its formula is  $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{H}$ .

Two methods were used in attempts to prepare the phenylacetate derivative.

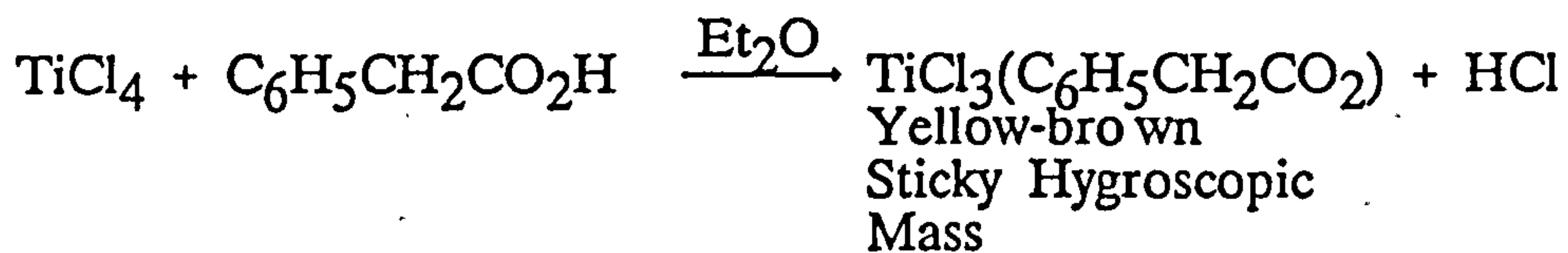
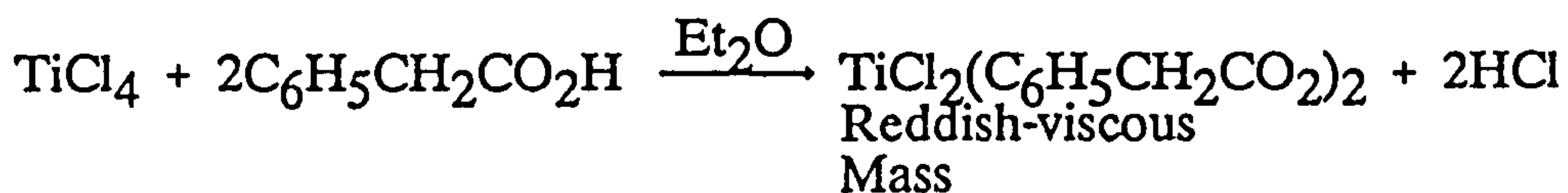
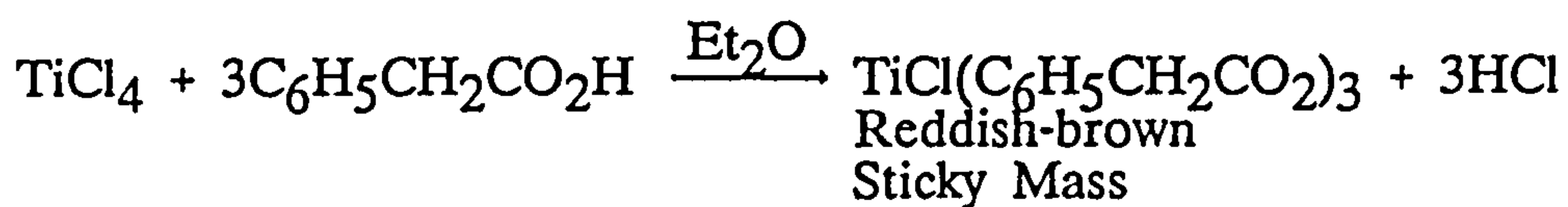
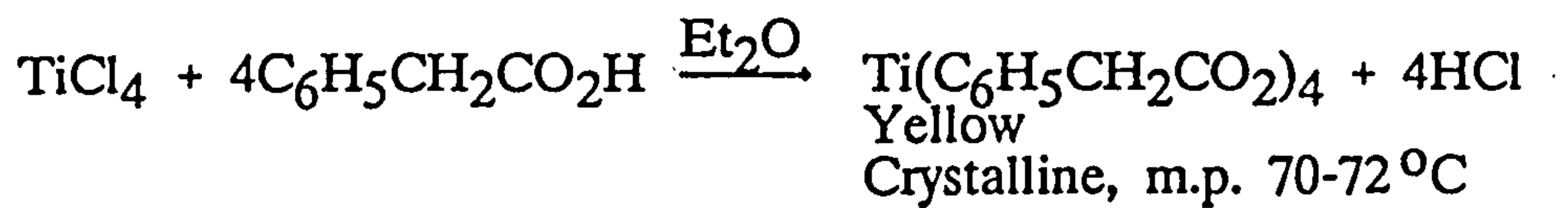
- (i) The reaction of excess titanium tetrachloride with a solution of phenylacetic acid in an organic solvent. Solvents used were benzene, dichloromethane, diethyl ether and tetrahydrofuran. Previous reported preparations of  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2)$  used diethyl ether as solvent.<sup>110</sup>
- (ii) Reaction of silver (or sodium) phenylacetate with titanium tetrachloride in diethyl ether.

After removal of solvent many of these reactions yielded only red-black oils. The metal carboxylate method produced black solids. Some orange and yellow solids were isolated from dichloromethane solution but the solids turned green or black almost immediately.

It appears that reduction of the titanium (IV) occurs with possible cleavage of the phenylacetic acid. It is difficult to determine how this reduction occurs due to the intractability of the products.

The reduction is so facile that Jaura's report<sup>(10)</sup> of the synthesis of  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2)$  must be regarded as doubtful. The claim was based only on titanium and chlorine analyses of what appears to be an inhomogenous product obtained from diethyl ether solution.

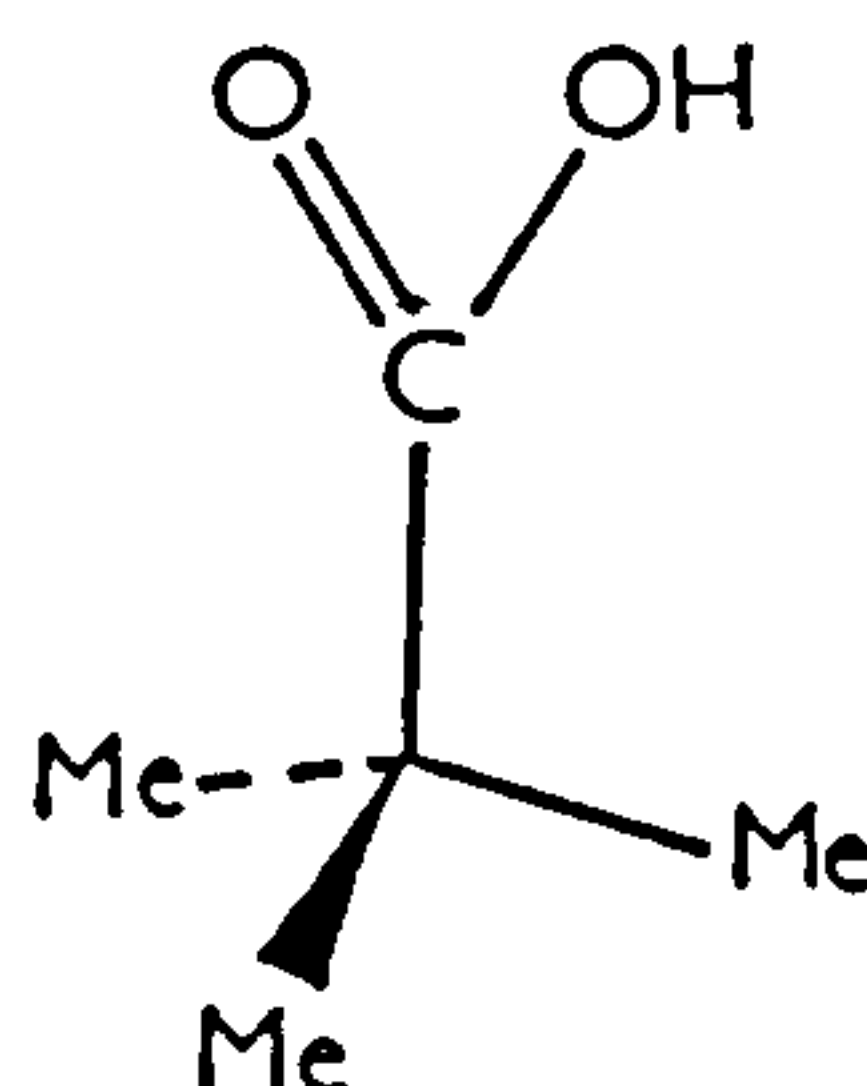
Reaction of titanium tetrachloride with phenylacetic acid (from ref. 110).





## PREPARATION OF $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$

Pivalic acid (2,2, dimethylpropanoic acid) is a colourless crystalline solid which melts at  $35.5^\circ\text{C}$ . Its  $\text{p}K_a$  is 5.01 at  $25^\circ\text{C}$ . The structure of pivalic acid is shown below:



The titanium pivalate was prepared by reaction of excess titanium tetrachloride with a benzene solution of pivalic acid. The red solution was heated for one hour and the volume of solvent reduced until yellow solid precipitated. The yellow solid was filtered off and washed with petroleum ether (b.p.  $60-80^\circ\text{C}$ ). It may be recrystallised from benzene forming rod shaped yellow crystals.

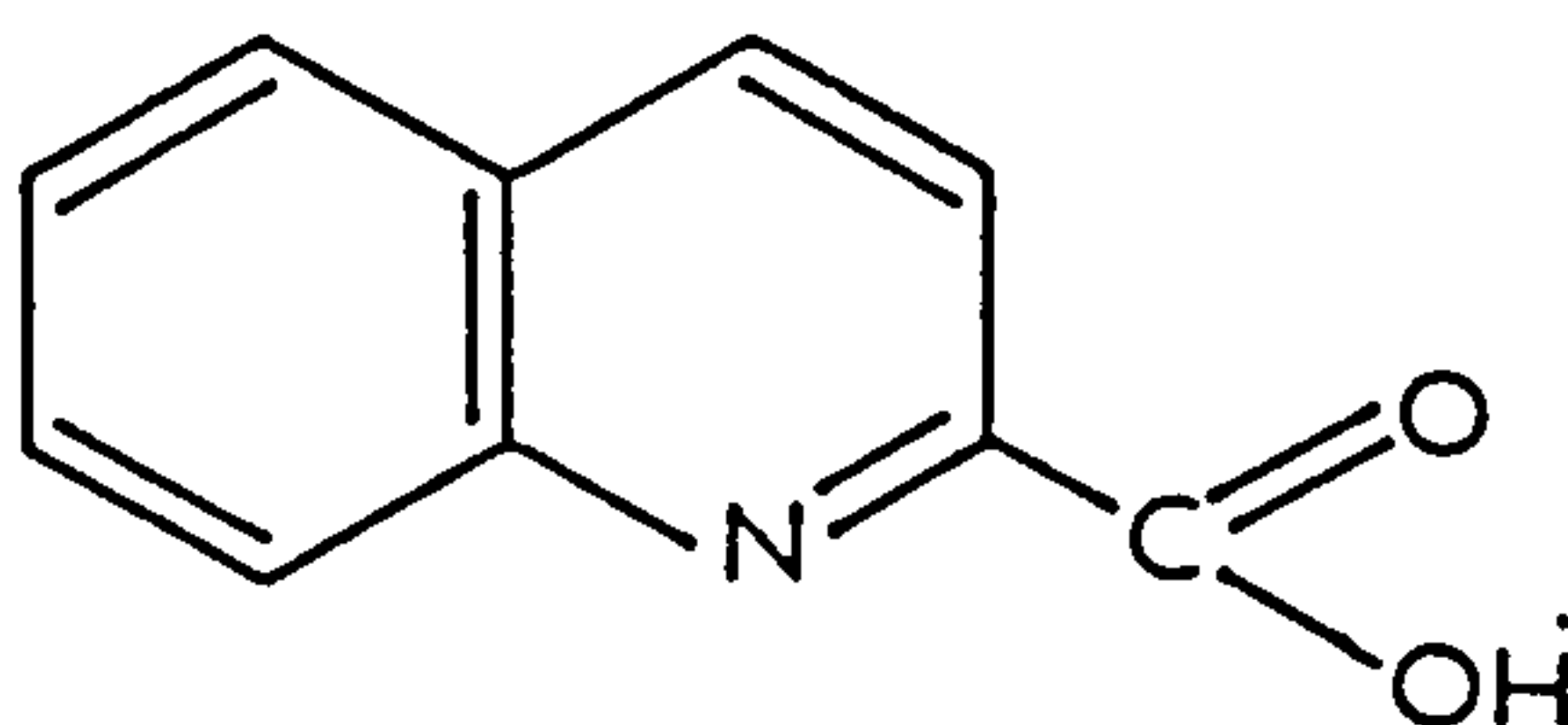
The  $^1\text{H}$  NMR spectrum of the pivalate contains multiple resonances at 1.1 p.p.m. - 1.5 p.p.m characteristic of the protons of the methyl groups. This spectrum is discussed in detail in Chapter 3 (p95-101).

The infra-red spectrum of the product has four bands due to carboxyl groups. The bands at  $1643\text{cm}^{-1}$  and  $1553\text{cm}^{-1}$  are assigned to  $\nu(\text{CO}_2)_{\text{asym}}$  vibrations and the bands at  $1508\text{ cm}^{-1}$  and  $1428\text{ cm}^{-1}$  to  $\nu(\text{CO}_2)_{\text{sym}}$  vibrations. The resulting  $\Delta$  values are  $135\text{cm}^{-1}$  and  $125\text{cm}^{-1}$  indicating the presence of two kinds of chelating and/or bridging carboxylate groups. Bands at  $458\text{cm}^{-1}$ ,  $403\text{cm}^{-1}$  and  $323\text{cm}^{-1}$  are assigned to Ti-Cl vibrations.

The infra-red spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  is discussed in more detail in Chapter 3 (p95).

### PREPARATION OF $\text{TiCl}_3(\text{C}_9\text{H}_6\text{NCO}_2)$

2 - Quinolinecarboxylic acid is a white solid which melts at 155 - 157 °C. Its  $\text{pK}_a$  at 25 °C is 4.92. When heated the acid decomposes forming quinoline<sup>(137)</sup>. The structure of 2 - quinolinecarboxylic acid is shown below:



This acid was used as it is possible that the nitrogen of the quinoline may coordinate to the titanium as well as the carboxyl group. It is also possible that the coordination of the nitrogen could force the formation of a monodentate carboxylate. Such a species would be of considerable interest as reaction with another metal centre could produce bimetallic compounds.

The carboxylate was prepared by reaction of excess titanium tetrachloride with 2 - quinolinecarboxylic acid in benzene. A yellow solid precipitated immediately. The suspension was then heated for six hours, the solid filtered off and washed with petroleum ether (b.p. 60 -80 °C). It was then dried *in vacuo* at room temperature.

The  $^1\text{H}$  NMR of the yellow solid has one resonance at 7.37 p.p.m. due to the ring protons.

The infra-red spectrum of the product contains four bands in the carboxylate stretching region. These are at 1615cm<sup>-1</sup>, 1600cm<sup>-1</sup>, 1585cm<sup>-1</sup> and 1428cm<sup>-1</sup>. The bands at 1615cm<sup>-1</sup> and 1600cm<sup>-1</sup> are assigned as ring vibrations. The band at 1585cm<sup>-1</sup> is assigned as  $\nu(\text{CO}_2^-)_{\text{asym}}$  and the band at 1428cm<sup>-1</sup> as  $\nu(\text{CO}_2^-)_{\text{sym}}$ . The resulting  $\Delta$  value is 157cm<sup>-1</sup>. This may indicate the presence of bridging and/or chelating carboxylate groups according to the Deacon and Phillips criteria(57).

Infra-red bands at 390cm<sup>-1</sup> and 250cm<sup>-1</sup> are tentatively assigned to Ti-Cl vibrations. The band at 415cm<sup>-1</sup> is assigned to out of plane ring deformations and the band at 280cm<sup>-1</sup> may be due to Ti-N vibrations(56).

It appears that the nitrogen is coordinated to the titanium centre. The carboxylate group may be bridging two titanium atoms. The insolubility of the product suggests it is a polymer. An X-ray structural study will be needed to discover the actual coordination of the compound however.

### PREPARATION OF $\text{TiCl}_3$ (o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)

o - Toluic acid (2 - methylbenzoic acid) is a white powder which melts at 107 - 8.°C. Its pK<sub>a</sub> at 25 °C is 3.9.

The o - toluate was prepared by addition of excess titanium tetrachloride to a toluene solution of o - toluic acid. An orange suspension formed and was heated at 100 °C for two hours. The resulting yellow solid was filtered off, washed with petroleum ether, and dried *in vacuo* at room temperature.

The compound is insoluble in most organic solvents. It is slightly soluble in CH<sub>2</sub>Cl<sub>2</sub>. It was characterised by elemental analysis, <sup>1</sup>H NMR spectra and



infra-red spectra. The analyses agree with the calculated values for  $\text{TiCl}_3$  ( $\text{o-CH}_3\text{C}_6\text{H}_4\text{CO}_2$ ).

The  $^1\text{H}$  NMR spectrum of the yellow material contains two resonances. These are at 6.8 - 8.3 p.p.m. and 2.2 - 3.0 p.p.m. The resonances are broad because the compound was only sparingly soluble in  $\text{CD}_2\text{Cl}_2$ . The resonance at 6.8 - 8.3 p.p.m. is due to the protons on the phenyl ring. The resonance at 2 - 3 p.p.m. is due to the methyl group.

The infra-red spectrum of  $\text{TiCl}_3$  ( $\text{o-CH}_3\text{C}_6\text{H}_4\text{CO}_2$ ) has five bands in the carboxyl stretching region. These are at  $1600\text{cm}^{-1}$ ,  $1580\text{cm}^{-1}$ ,  $1550\text{cm}^{-1}$ ,  $1505\text{cm}^{-1}$  and  $1340\text{cm}^{-1}$ . The bands at  $1600\text{cm}^{-1}$  and  $1505\text{cm}^{-1}$  are assigned as ring vibrations. The band at  $1550\text{cm}^{-1}$  is assigned as  $\nu(\text{CO}_2)_{\text{asym}}$  and the band at  $1340\text{cm}^{-1}$  as  $\nu(\text{CO}_2)_{\text{sym}}$ . The resulting  $\Delta$  value is  $210\text{cm}^{-1}$ . According to the Deacon and Phillips criteria<sup>(57)</sup> this suggests that the carboxylate groups are in an unidentate bonding mode.

Bands at 420, 410, 380 and  $270\text{cm}^{-1}$  are assigned to Ti-Cl vibrations. The bands at  $420\text{cm}^{-1}$ ,  $410\text{cm}^{-1}$  and  $380\text{cm}^{-1}$  are probably due to terminal  $\nu(\text{Ti-Cl})$  stretching vibrations. The band at  $270\text{cm}^{-1}$  has a contribution from bridging Ti-Cl vibrations.



## PREPARATION OF $\text{TiCl}_3(\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$

p - Toluic acid (4 - methylbenzoic acid) is a white solid which melts at  $181^\circ\text{C}$ . Its  $\text{p}K_a$  is 4.37.

The p - toluate was prepared by addition of excess titanium tetrachloride to a benzene solution of p - toluic acid. The red solution was heated at  $70^\circ\text{C}$  for 2 hours and the volume of solvent reduced. A yellow solid precipitated from the solution. The supernatant liquid was removed and the yellow solid washed with petroleum ether (b.p.  $60 - 80^\circ\text{C}$ ) and dried *in vacuo* at room temperature.

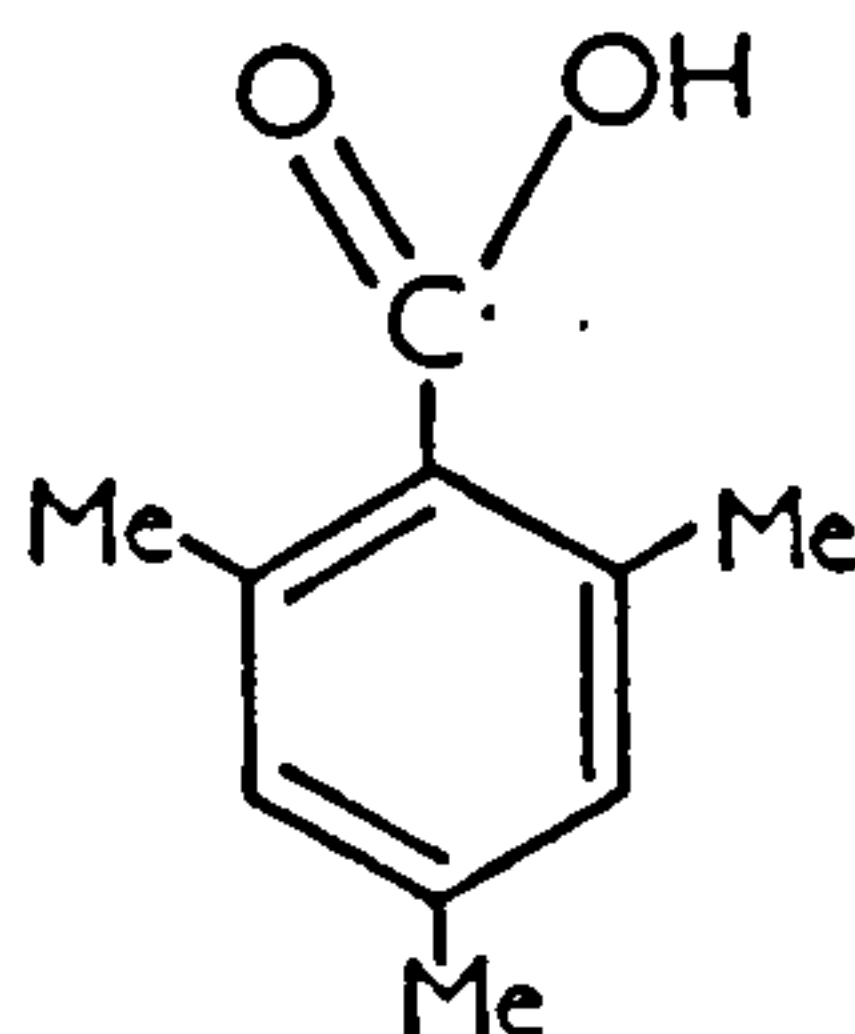
The  $^1\text{H}$  NMR spectrum of the solid contains resonances at 7.39 p.p.m., 8.0 p.p.m. and 2.49 p.p.m. The resonances at 7.39 p.p.m. and 8.0 p.p.m. are due to the ring protons and the resonance at 2.49 p.p.m., is due to the methyl group.

The carbonyl stretching region in the infra-red spectrum of  $\text{TiCl}_3(\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$  contains five bands. These are at  $1610\text{cm}^{-1}$ ,  $1580\text{cm}^{-1}$ ,  $1530\text{cm}^{-1}$ ,  $1505\text{cm}^{-1}$  and  $1410\text{cm}^{-1}$ . The bands at  $1610\text{cm}^{-1}$  and  $1505\text{cm}^{-1}$  are assigned as ring vibrations. The band at  $1530\text{cm}^{-1}$  may be assigned as  $\nu(\text{CO}_2)_{\text{asym}}$  and the band at  $1410\text{cm}^{-1}$  as  $\nu(\text{CO}_2)_{\text{sym}}$ . The resulting  $\Delta$  value is  $120\text{cm}^{-1}$  which according to the Deacon and Phillips criteria<sup>(57)</sup> indicates the presence of chelating and/or bridging carboxylate groups. This value contrasts with that of the ortho-toluic acid derivative ( $210\text{cm}^{-1}$ ). The difference may be due to steric hindrance from the methyl group in the ortho compound preventing the carboxylate chelating or bridging.

Bands at  $400\text{cm}^{-1}$ ,  $330\text{cm}^{-1}$  and  $295\text{cm}^{-1}$  are assigned to Ti-Cl vibrations.

## PREPARATION OF $\text{TiCl}_3[\text{C}_6\text{H}_2(\text{CH}_3)_3\text{CO}_2]$

2,4,6 - Trimethylbenzoic acid (mesitoic acid) is a white powder which melts at  $155^\circ\text{C}$ . Its  $\text{p}K_a$  at  $25^\circ\text{C}$  is 4.43. The structure of 2,4,6 - trimethylbenzoic acid is shown below:



The carboxylate was prepared by addition of excess titanium tetrachloride to a dichloromethane solution of 2,4,6 - trimethylbenzoic acid. The red solution was then heated for 5 hours and allowed to cool. Addition of petroleum ether (b.p.  $100-120^\circ\text{C}$ ) caused an orange solid to precipitate. The solid was filtered off, washed with petroleum ether (b.p.  $60-80^\circ\text{C}$ ) and dried *in vacuo* at room temperature. When benzene or toluene are used as solvent no solid products could be isolated.

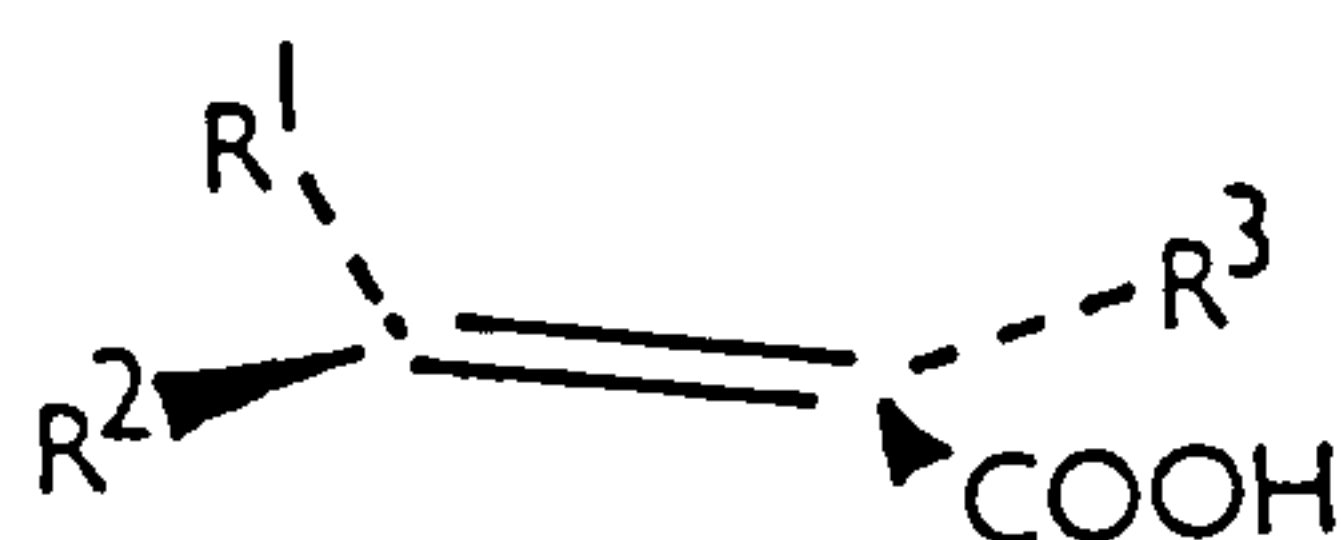
The  $^1\text{H}$  NMR spectrum of the orange solid has two resonances due to  $\text{TiCl}_3[\text{C}_6\text{H}_2(\text{CH}_3)_3\text{CO}_2]$  and resonances due to slight contamination by petroleum ether. The resonances due to  $\text{TiCl}_3[\text{C}_6\text{H}_2(\text{CH}_3)_3\text{CO}_2]$  are at 6.87 p.p.m. and 2.26 p.p.m. The resonance at 6.87 p.p.m. is due to the ring protons and the resonance at 2.26 p.p.m. due to the three methyl groups. The petroleum ether gives small resonances centred around 1 p.p.m.

The infra-red spectrum of the product contains four bands in the carbonyl stretching region. These are at  $1610\text{cm}^{-1}$ ,  $1595\text{cm}^{-1}$ ,  $1575\text{cm}^{-1}$  and

1485cm<sup>-1</sup>. The band at 1610cm<sup>-1</sup> is assigned to ring vibrations. The band at 1595cm<sup>-1</sup> may be assigned as  $\nu(\text{CO}_2^-)_{\text{asym}}$  and the band at 1485cm<sup>-1</sup> as  $\nu(\text{CO}_2^-)_{\text{sym}}$ . The resulting  $\Delta$  value is 110cm<sup>-1</sup>. According to the Deacon and Phillips criteria<sup>(57)</sup> this indicates the presence of bridging and/or chelating carboxylate groups. Bands at 405cm<sup>-1</sup>, 390cm<sup>-1</sup> and 300cm<sup>-1</sup> are assigned to Ti - Cl vibrations. This compound differs from the o-toluate in that despite having methyl groups next to the carboxyl group the  $\Delta$  value indicates the carboxylate is bridging and/or chelating. The  $\Delta$  value for the o-toluate indicates the carboxylate group is unidentate.

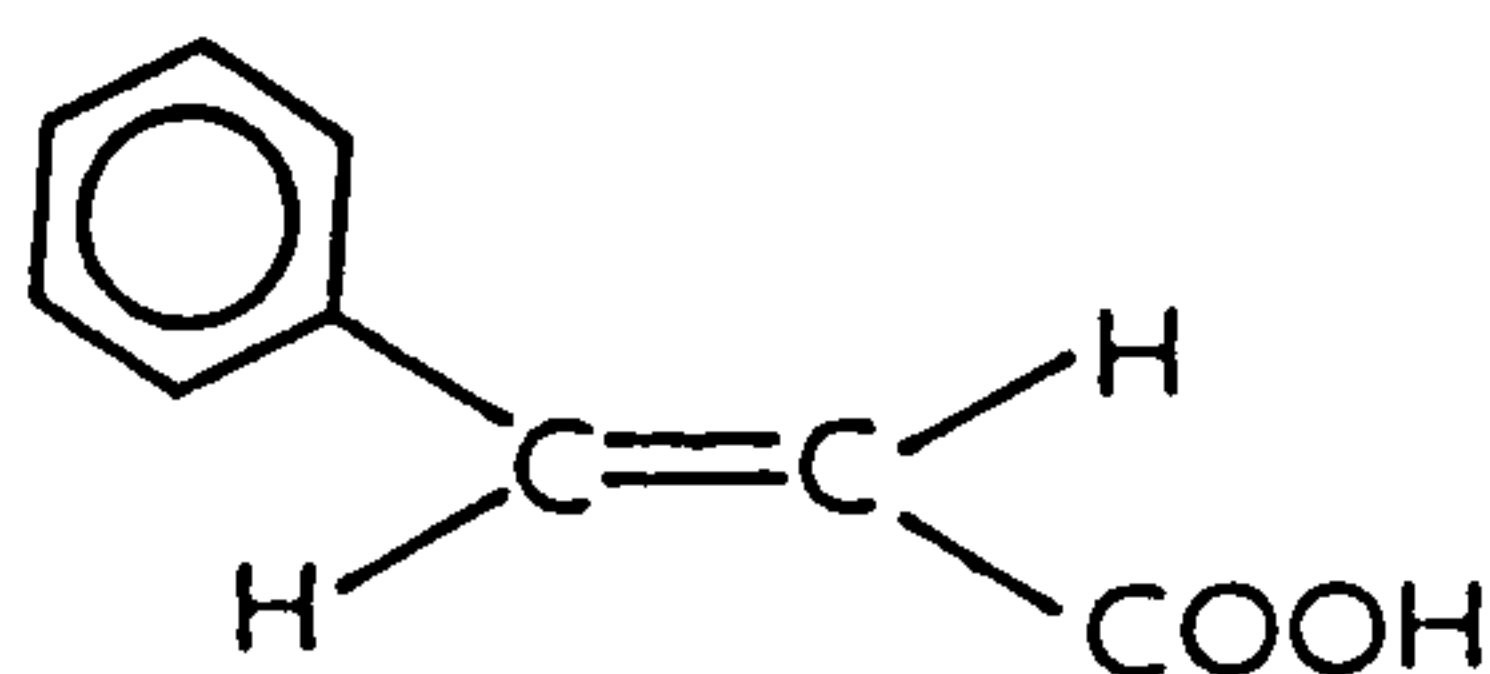
### $\alpha$ - $\beta$ - UNSATURATED CARBOXYLATES

Some  $\alpha$ ,  $\beta$  - unsaturated carboxylic acids have been used in our preparative experiments. These acids have a carbon - carbon double bond which has the potential to coordinate to the metal centre. This would produce very interesting structures. An  $\alpha$ ,  $\beta$  - unsaturated carboxylic acid has the general structure shown below:

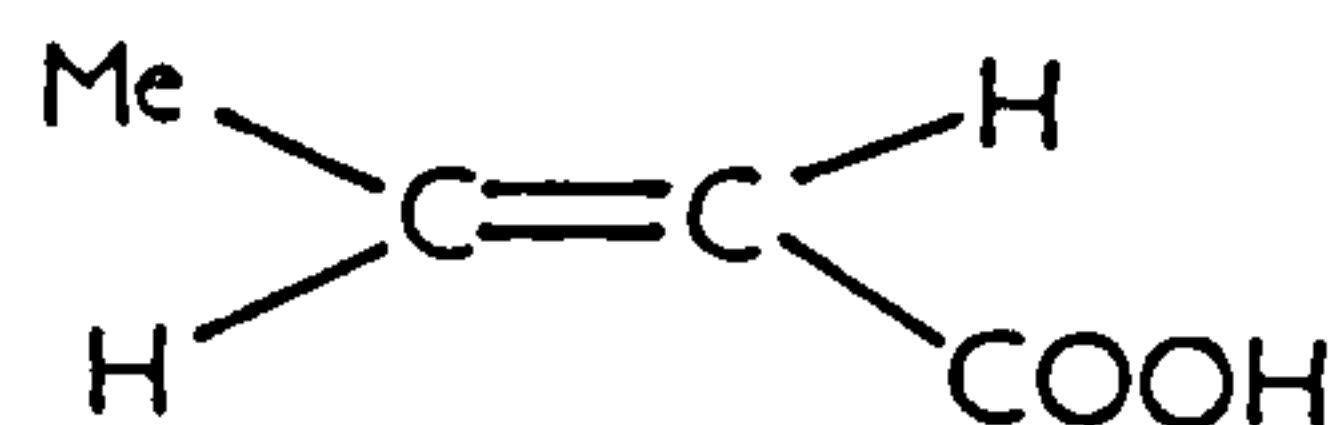


Carboxylates have been prepared from cinnamic acid (3 - phenyl - 2 - propenoic acid) and crotonic acid (*trans* - 2 - butenoic acid). The structures of these acids are shown overleaf:





Cinnamic acid



Crotonic acid

The monocarboxylates were made by reaction of a slight excess of titanium tetrachloride with a dichloromethane solution of the acid at 0°C. Attempts were made to prepare the crotonate from benzene or toluene solution. Orange solids were obtained which contained solvent. The solvent could be driven off giving a yellow solid by heating the orange solid in a vacuum. Unfortunately the yellow solid proved to be inhomogenous.

Using dichloromethane as solvent, a yellow solid was obtained using crotonic acid and a red solid using cinnamic acid. The solids were obtained by reducing the volume of solution until precipitation occurred. The solid was filtered off, washed with hexane and dried *in vacuo* at room temperature.

Infra-red data for the compounds are reported in Table 2.1. The  $\Delta$  values of 155cm<sup>-1</sup> for both compounds indicate the possible presence of chelating and/or bridging carboxylates(57).



**Table 2.1: Infra-red data for the carboxylate stretching region of  $\alpha$ ,  $\beta$  - unsaturated carboxylates.**

	<b>TiCl<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>CH = CHCO<sub>2</sub>)</b>	<b>TiCl<sub>3</sub>(CH<sub>3</sub>CH = CHCO<sub>2</sub>)</b>
	<b>(cm<sup>-1</sup>)</b>	<b>(cm<sup>-1</sup>)</b>
C = C vibration	1620	1635
$\nu(\text{CO}_2^-)_{\text{asym}}$	1545	1580
$\nu(\text{CO}_2^-)_{\text{sym}}$	1390	1425
$\Delta$	155	155

The <sup>1</sup>H NMR spectrum of the crotonate contains three resonances. These are at 2.2 p.p.m., 6.25 p.p.m. and 7.75 p.p.m. The resonance at 2.2 p.p.m. is due to the methyl group, the resonance at 7.75 p.p.m. can be assigned to the adjacent proton and the resonance at 6.25 p.p.m. is due to the CH proton next to the carboxyl group.

The <sup>1</sup>H NMR spectrum of the cinnamate has four resonances. These are at 7.7 p.p.m, 7.53 p.p.m., 7.3 p.p.m. and 6.65 p.p.m. The resonance at 6.65 p.p.m. is due to the CH proton next to the carboxyl group. The other CH proton resonates at 7.7 p.p.m. and the resonances at 7.53 p.p.m. and 7.3 p.p.m. are due to phenyl protons.

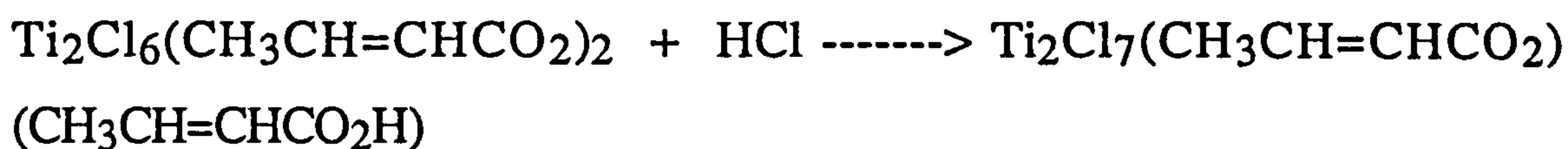
### **THE STRUCTURE OF Ti<sub>2</sub>Cl<sub>7</sub> (CH<sub>3</sub>CH=CHCO<sub>2</sub>) (CH<sub>3</sub>CH=CHCO<sub>2</sub>H)**

An attempt was made to prepare crystals of TiCl<sub>3</sub>(CH<sub>3</sub>CH=CHCO<sub>2</sub>) suitable for an X-ray structural examination. The yellow titanium

dissolved in dichloromethane and long yellow needle-like crystals were grown by the liquid diffusion method using hexane as a precipitant. Upon solving the structure, the crystals were found to be  $\text{Ti}_2\text{Cl}_7(\text{CH}_3\text{CH}=\text{CHCO}_2)(\text{CH}_3\text{CH}=\text{CHCO}_2\text{H})$ .

The new species had formed during the crystallisation of  $\text{TiCl}_3(\text{CH}_3\text{CH}=\text{CHCO}_2)$ . It is possible that the crotonic acid/titanium tetrachloride adduct was present originally, and that this adduct reacted with the carboxylate forming the new species. However no evidence for the presence of  $\text{TiCl}_4$ ,  $\text{CH}_3\text{CH}=\text{CHCO}_2\text{H}$  was found in the infra-red,  $^1\text{H}$  NMR spectra, or elemental analysis of the starting material. The  $\Delta$  value found from the infra-red spectrum of the starting material was  $155\text{cm}^{-1}$  indicating the presence of bridging and/or chelating carboxylate ligands. The adduct would only give one infra-red band in the carbonyl stretching region and no  $\Delta$  value would be observed.

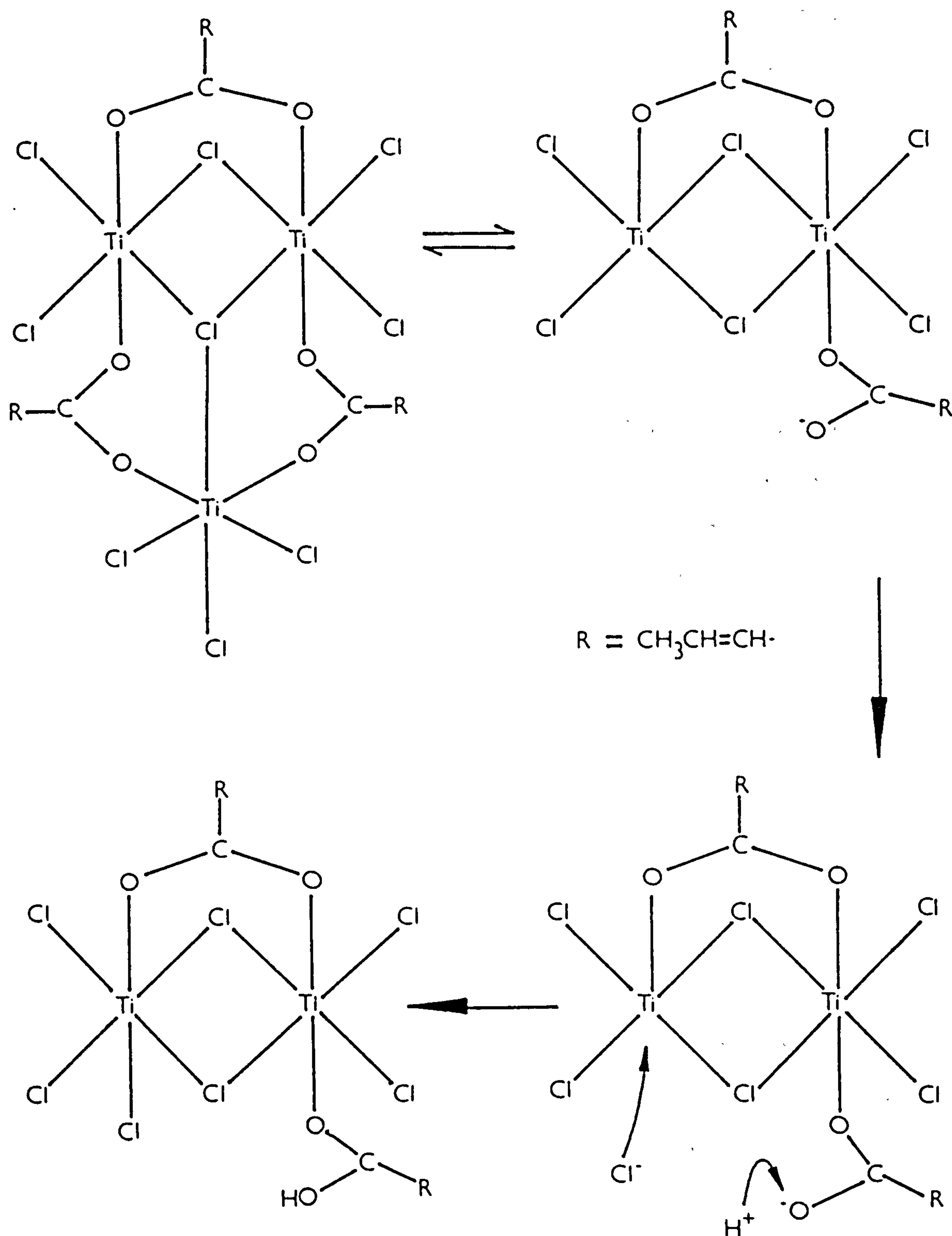
An alternative explanation is the presence of very small amounts of water in the hexane precipitant. The water reacted with some of the titanium chloro - species present forming oxo - compounds and  $\text{HCl}$ . The oxo - compounds precipitated, some white deposits were observed, and the  $\text{HCl}$  attacked carboxylate dimers forming the new species.



$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  has a trimeric structure in the solid state, and it has been proposed that the carboxylate dissociates into dimers and five coordinate species in solution (chapter 3). It is possible that the crotonate has similar behavior, when the initial dissociation takes place the molecule

becomes available for attack by HCl. A possible scheme for the reaction is shown in Figure 2.1:

**Figure 2.1:** A possible scheme for formation of  $\text{Ti}_2\text{Cl}_7(\text{CH}_3\text{CH}=\text{CHCO}_2) (\text{CH}_3\text{CH}=\text{CHCO}_2\text{H})$





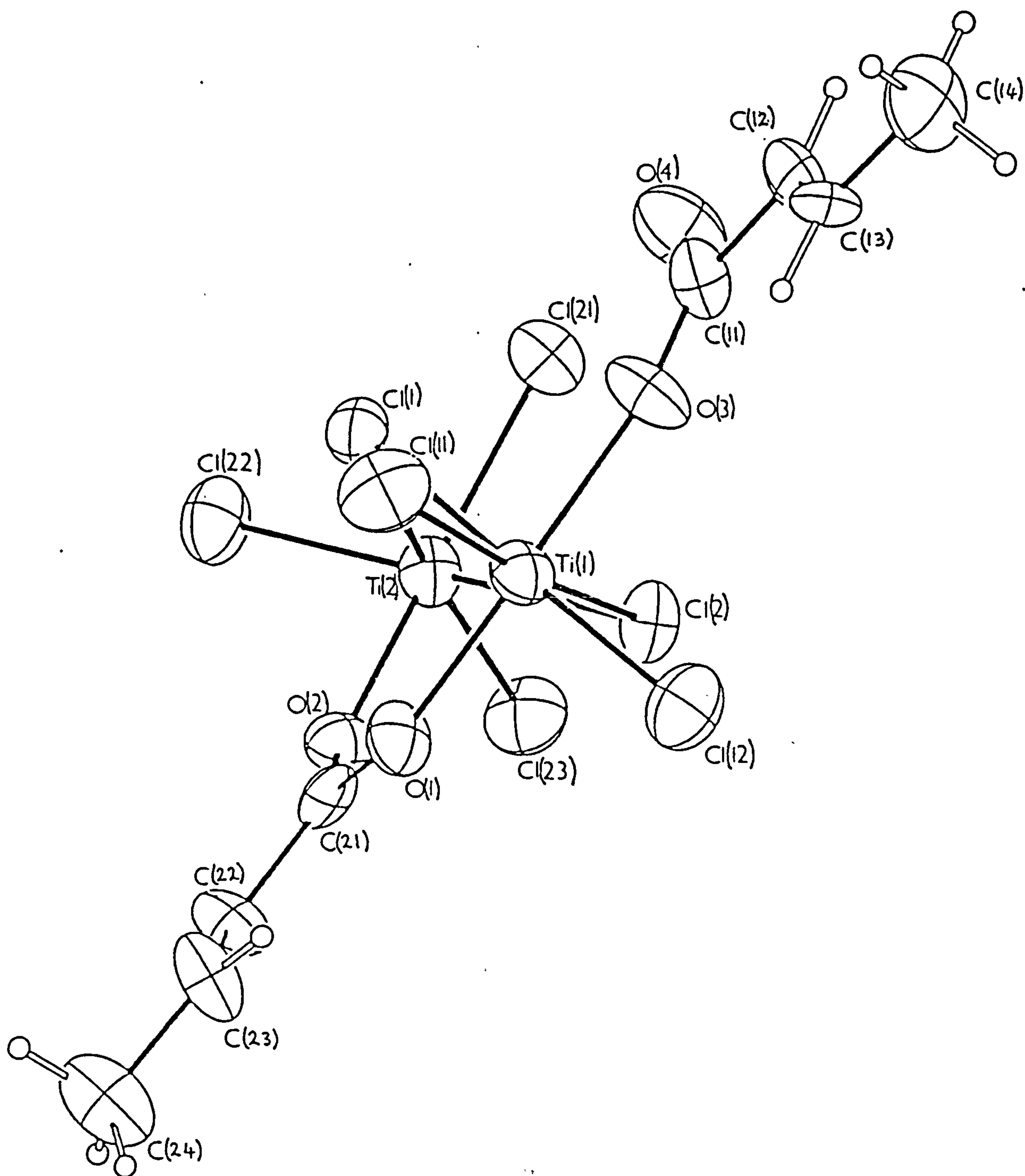
The molecule  $\text{Ti}_2\text{Cl}_7(\text{CH}_3\text{CH}=\text{CHCO}_2)(\text{CH}_3\text{CH}=\text{CHCO}_2\text{H})$  is dimeric, the two titanium atoms being linked by a carboxylate bridge and two chlorine bridges. Each titanium has pseudo-octahedral coordination with all equatorial positions occupied by chlorine atoms. Two views of the structure and the atom numbering scheme are shown in Figures 2.2 and 2.3 and Tables 2.2 and 2.3 contain bond lengths and angles respectively for the complex.

One chlorine atom on Ti (2) is *trans* to an oxygen of the bridging carboxylate, the other oxygen atom of the carboxylate bridge is *trans* to the 'carbonyl' oxygen atom of the coordinated carboxylic acid.

The carboxyl carbon of the bridging carboxylate is almost trigonal, all bond angles are around  $120^\circ$ . The angles around the carboxyl carbon of the coordinated acid are closer to those of the free acid(138) In particular the C(22) - C(21) -O(4) angle of  $111.5^\circ$  shows that O(4) is the hydroxyl oxygen. In the free acid this angle is  $115^\circ$ (138) The C(21) - O(4) bond length of  $1.334\text{\AA}$  compared to the C(21) -O(3) bond length of  $1.222\text{\AA}$  also indicates the presence of a proton on O(4).

The  $\text{Ti}_2\text{Cl}_6$  central unit of the molecule is similar to that found in many titanium tetrachloride adducts such as  $[\text{TiCl}_4.\text{POCl}_3]_2$ (139) or  $[\text{TiCl}_4.\text{EtOAc}]_2$ (82). The Ti-Cl-Ti angles of the bridges are less than the ideal  $90^\circ$  showing elongation of the bridges. The Cl-Ti-Cl angles of the terminal equatorial chlorines have opened to about  $100^\circ$  as predicted by the work of Hoffmann.(140). The terminal and bridging chlorines are staggered, presumably to avoid interaction with each other.

The complex has some similarities to the bimetallic compound  $\text{TiMgCl}_5(\text{CH}_2\text{ClCO}_2)(\text{CH}_2\text{ClCOOC}_2\text{H}_5)_3$  prepared by Bart and coworkers.<sup>(12)</sup> The bimetallic compound has the same triply bridging unit composed of two chlorine bridges and a carboxylate bridge joining the titanium and magnesium atoms. All terminal chlorines in the bimetallic complex have approximately equal Ti-Cl bond lengths, however in the titanium crotonate compound the bond to the chlorine *trans* to the bridging carboxylate is longer than the others. This may indicate that this chlorine is  $\text{Cl}^-$  from attack of HCl on  $\text{Ti}_2\text{Cl}_6(\text{CH}_3\text{CH}=\text{CHCO}_2)_2$ .



**Figure 2.2:** The Structure of  $\text{Ti}_2\text{Cl}_7(\text{CH}_3\text{CH}=\text{CHCO}_2)(\text{CH}_3\text{CH}=\text{CHCO}_2\text{H})$

Figure 2.3: The Structure of  $\text{Ti}_2\text{Cl}_7(\text{CH}_3\text{CH}=\text{CHCO}_2)(\text{CH}_3\text{CH}=\text{CHCO}_2\text{H})$

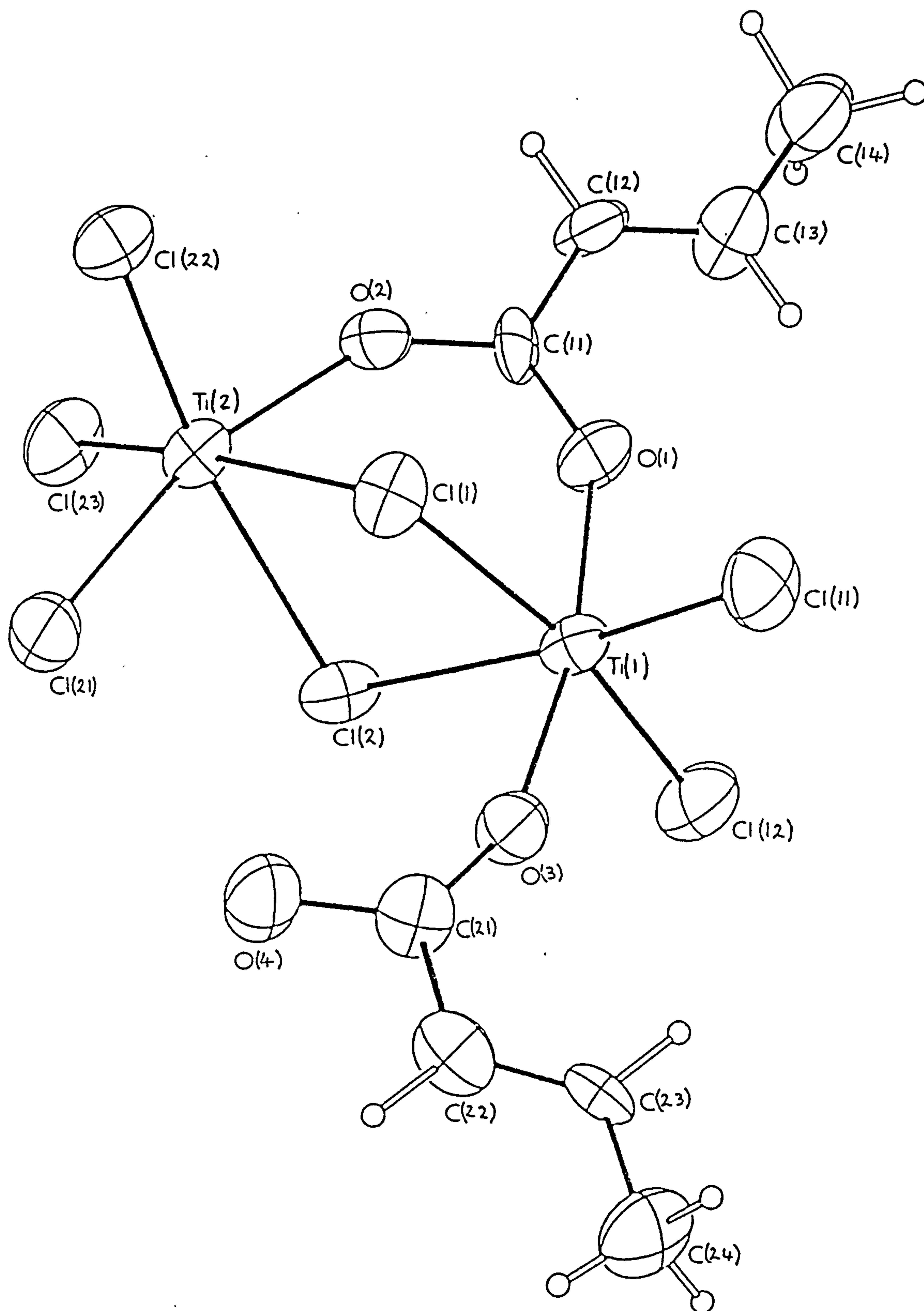




Table 2.2: Bond lengths(Å)

Ti(1)-C1(1)	2.450(5)	Ti(1)-C1(2)	2.494(5)
Ti(1)-C1(11)	2.197(6)	Ti(1)-C1(12)	2.205(5)
Ti(1)-O(1)	1.836(10)	Ti(1)-O(3)	1.960(12)
Ti(2)-C1(1)	2.524(5)	Ti(2)-C1(2)	2.528(4)
Ti(2)-C1(21)	2.265(5)	Ti(2)-C1(22)	2.190(5)
Ti(2)-C1(23)	2.189(6)	Ti(2)-O(2)	2.008(11)
O(1)-C(11)	1.276(17)	O(2)-C(11)	1.247(16)
O(3)-C(21)	1.222(22)	O(4)-C(21)	1.334(20)
C(11)-C(12)	1.461(23)	C(12)-C(13)	1.264(23)
C(13)-C(14)	1.532(26)	C(21)-C(22)	1.456(24)
C(22)-C(23)	1.338(22)	C(23)-C(24)	1.499(23)

Table 2.3: Bond angles (deg.)

C1(1)-Ti(1)-C1(2)	80.2(2)	C1(1)-Ti(1)-C1(11)	91.8(2)
C1(2)-Ti(1)-C1(11)	172.0(2)	C1(1)-Ti(1)-C1(12)	167.7(2)
C1(2)-Ti(1)-C1(12)	86.0(2)	C1(11)-Ti(1)-C1(12)	99.9(2)
C1(1)-Ti(1)-O(1)	85.5(3)	C1(2)-Ti(1)-O(1)	84.3(4)
C1(11)-Ti(1)-O(1)	95.1(4)	C1(12)-Ti(1)-O(1)	96.7(3)
C1(1)-Ti(1)-O(3)	85.4(3)	C1(2)-Ti(1)-O(3)	87.3(4)
C1(11)-Ti(1)-O(3)	92.2(4)	C1(12)-Ti(1)-O(3)	90.7(3)
O(1)-Ti(1)-O(3)	168.5(4)	C1(1)-Ti(2)-C1(2)	78.3(2)
C1(1)-Ti(2)-C1(21)	87.6(2)	C1(2)-Ti(2)-C1(21)	85.9(2)
C1(1)-Ti(2)-C1(22)	90.3(2)	C1(2)-Ti(2)-C1(22)	168.2(2)
C1(21)-Ti(2)-C1(22)	96.8(2)	C1(1)-Ti(2)-C1(23)	169.0(2)
C1(2)-Ti(2)-C1(23)	91.4(2)	C1(21)-Ti(2)-C1(23)	95.7(2)
C1(22)-Ti(2)-C1(23)	99.7(2)	C1(1)-Ti(2)-O(2)	82.1(3)
C1(2)-Ti(2)-O(2)	81.1(3)	C1(21)-Ti(2)-O(2)	164.8(3)
C1(22)-Ti(2)-O(2)	94.5(3)	C1(23)-Ti(2)-O(2)	92.4(3)
Ti(1)-C1(1)-Ti(2)	96.9(2)	Ti(1)-C1(2)-Ti(2)	96.0(2)
Ti(1)-O(1)-C(11)	141.9(10)	Ti(2)-O(2)-C(11)	143.6(10)
Ti(1)-O(3)-C(21)	152.6(11)	O(1)-C(11)-O(2)	120.7(14)
O(1)-C(11)-C(12)	119.5(12)	O(2)-C(11)-C(12)	119.9(13)
C(11)-C(12)-C(13)	123.1(14)	C(12)-C(13)-C(14)	124.4(15)
O(3)-C(21)-O(4)	126.0(15)	O(3)-C(21)-C(22)	122.5(15)
O(4)-C(21)-C(22)	111.5(15)	C(21)-C(22)-C(23)	121.2(16)
C(22)-C(23)-C(24)	122.8(16)		

## ATTEMPTED PREPARATION OF $[\text{TiCl}_3\{(\text{CH}_3)_3\text{CCOS}\}]$

Attempts were made to prepare  $[\text{TiCl}_3\{(\text{CH}_3)_3\text{CCOS}\}]$ . A slight excess of titanium tetrachloride was added to a dichloromethane solution of thiopivalic acid. The resulting red solution was stirred for one hour after which a dark yellow solid precipitated. The supernatant liquid was removed and the solid washed with petroleum ether (b.p. 60 - 80 °C). It was then dried *in vacuo*.

The infra-red spectrum of the dark yellow solid has a band at 2520 $\text{cm}^{-1}$  due to S-H vibrations. The carbonyl band is at 1555 $\text{cm}^{-1}$ . The shift of this band relative to the free acid indicates that the carbonyl oxygen is bonding to titanium.

The  $^1\text{H}$  NMR spectrum of the solid contains a resonance at 0.9 p.p.m., due to the methyl groups.

It appears that the adduct  $\text{TiCl}_4 \cdot (\text{CH}_3)_3\text{CCOSH}$  has been formed rather than the carboxylate  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCOS}]$ . This is shown by the presence of S-H bands in the infra-red spectrum. The elemental analysis of the solid gives values close to those calculated for  $\text{TiCl}_4 \cdot (\text{CH}_3)_3\text{CCOSH}$ . The shift of the carbonyl band in the infra-red spectrum is evidence that the acid binds to titanium through the carbonyl oxygen in a similar way to ethyl acetate in  $[\text{TiCl}_4 \cdot \text{EtOAc}]_2$ .



## PREPARATION OF $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_3(\text{C}_6\text{H}_5\text{CO}_2)$

$\text{Ti}[\text{OCH}(\text{CH}_3)_2]_3(\text{C}_6\text{H}_5\text{CO}_2)$  was prepared by addition of  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  to a benzene solution of benzoic acid. The resulting colourless solution was heated at reflux temperature for eight hours. A cream coloured oil was produced. The oil was recrystallised from hexane to give a white solid.

The infra-red spectrum of the solid contains bands due to both alkoxide and carboxylate groups. Bands at 1320, 1135, 850, 815, 475 and 360 $\text{cm}^{-1}$  are due to the alkoxide groups. A band at 620 $\text{cm}^{-1}$  is due to  $\nu(\text{Ti-O})$  vibrations of the alkoxide groups. The band at 1420 $\text{cm}^{-1}$  may be assigned to  $\nu(\text{CO}_2^-)_{\text{sym}}$ ;  $\nu(\text{CO}_2^-)_{\text{asym}}$  is assigned to either the band at 1560 $\text{cm}^{-1}$  or the band at 1540 $\text{cm}^{-1}$ . The resulting  $\Delta$  value is either 140 $\text{cm}^{-1}$  or 120 $\text{cm}^{-1}$ . Bands at 1600 $\text{cm}^{-1}$  and 1490 $\text{cm}^{-1}$  are due to the aromatic ring of the benzoate. The possible  $\Delta$  values are consistent with the presence of a bridging and/or chelating carboxylate group<sup>(57)</sup>

The  $^1\text{H}$  NMR spectrum of the product contains resonances at 8.2 p.p.m., 7.5 p.p.m., 5.09 p.p.m., and 1.3 p.p.m. The resonances at 8.2 p.p.m. and 5.09 p.p.m. are due to protons on the ring of the  $\text{C}_6\text{H}_5\text{CO}_2^-$  group. The resonance at 1.3 p.p.m. is due to the methyl groups of the alkoxides and the resonance at 5.09 p.p.m. is due to the CH groups of the alkoxides. The ration of benzoate protons to iso-propoxide protons is 5:21 indicating that alkoxide and carboxylate groups are present in the ratio 3 alkoxides : 1 carboxylate.

The white solid is  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_3(\text{C}_6\text{H}_5\text{CO}_2)$ . This is confirmed by its elemental analysis which gives values for Ti, C and H analyses very close to those calculated for  $\text{TiC}_{16}\text{H}_{26}\text{O}_5$ .

Cryoscopic molecular mass measurements show that the molecular mass of the compound in benzene solution increases with increasing concentration. (See Table 2.4).

The molecular mass of the monomeric  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_3 (\text{C}_6\text{H}_5\text{CO}_2)$  molecule is 345.9. It appears therefore that the complex dissociates in dilute solution and associates to form oligomers in more concentrated solutions.

**Table 2.4**                      **Variation of molecular mass with concentration for  $\text{Ti}(\text{OPri})_3(\text{C}_6\text{H}_5\text{CO}_2)$**

Concentration	Molecular Mass	N x Monomer
0.0214M	121.3	0.35
0.0972M	287.9	0.83
0.241M	516.91	1.49



### III. REACTIONS OF TITANIUM (IV) TRIS(CHLORO)MONO(CARBOXYLATES)

#### (i) Reactions of $\text{TiCl}_3(\text{RCO}_2)$ with tetrahydrofuran.

The reaction of  $\text{TiCl}_3(\text{RCO}_2)$  ( $\text{R} = \text{C}_6\text{H}_5, (\text{CH}_3)_3\text{C}$  and  $o - \text{CH}_3\text{C}_6\text{H}_4\text{CO}_2$ ) with THF was investigated by adding stoichiometric quantities of dry THF to solutions of the carboxylate. A variation was to dissolve the carboxylate in THF.

In the presence of excess dry THF the carboxylate groups are displaced and the adduct  $\text{TiCl}_4 \cdot 2\text{THF}$  formed. The formation of the adduct was confirmed by  $^1\text{H}$  NMR spectra and elemental analyses. The analyses for Ti, C, H and Cl of the yellow products agreed well with the calculated values for  $\text{TiCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$ . The  $^1\text{H}$  NMR spectra contained resonances at 2.06 p.p.m. and 4.46 p.p.m. Both resonances are multiplets. No resonances were observed due to carboxylate groups. The resonances at 2.06 and 4.46 p.p.m. were due to the protons of coordinated tetrahydrofuran.

The addition of stoichiometric amounts of dry THF to the carboxylate solutions caused the formation of ill defined black or red oils. However if the THF contains the slightest trace of water then the oxo-compound  $[\text{TiCl}_2(\text{RCO}_2)\text{THF}]_2\text{O}$  is produced. The formation of this complex was confirmed by comparison of its infra-red and  $^1\text{H}$  NMR spectra to those of a genuine sample of  $[\text{TiCl}_2(\text{RCO}_2)\text{THF}]_2\text{O}$ . The preparation of oxo-compounds is described in chapter 4. The carbon, hydrogen and titanium analyses of the product from the reaction of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with THF show it is  $\{\text{TiCl}_2[(\text{CH}_3)_3\text{CCO}_2]\text{THF}\}_2\text{O}$ .

It appears that titanium (IV) tris(chloro)monocarboxylates are vulnerable to attack by THF. In THF solution the carboxylate ligands are displaced and the adduct  $\text{TiCl}_4 \cdot 2\text{THF}$  formed. The addition of water stabilises the carboxylate by formation of an oxygen bridge between the titanium centres<sup>(128)</sup> so the carboxylate ligands are not displaced, and  $[\text{TiCl}_2(\text{RCO}_2)\text{THF}]_2\text{O}$  is formed.

## (ii) Reaction of $\text{TiCl}_3(\text{RCO}_2)$ complexes with THF and phenols

In an attempt to prepare a phenoxide bridged variant of the oxo-compound  $[\text{TiCl}_2(\text{RCO}_2)\text{L}]_2\text{O}$  several titanium (IV) tris(chloro)mono(carboxylates) were reacted with THF and phenol. Oxo-compounds are discussed in detail in chapter 4.

The product of the reaction between  $\{\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]\}$ , THF and phenol was an orange solid which analysed as  $\{\text{TiCl}_2[(\text{CH}_3)_3\text{CCO}_2]\text{THF}\}_2\text{OC}_6\text{H}_5$ . The infra-red spectrum of the solid has bands at  $1540\text{cm}^{-1}$  and  $1430\text{cm}^{-1}$  due to  $\nu(\text{CO}_2^-)_{\text{asym}}$  and  $\nu(\text{CO}_2^-)_{\text{sym}}$  respectively. The resulting  $\Delta$  value is  $110\text{cm}^{-1}$ . This indicates the presence of bridging and/or chelating carboxylates<sup>(57)</sup>.

Other bands of interest in the infra-red spectrum are at  $760\text{cm}^{-1}$ ,  $460\text{cm}^{-1}$ ,  $390\text{cm}^{-1}$  and  $250\text{cm}^{-1}$ . The bands at  $460\text{cm}^{-1}$  and  $250\text{cm}^{-1}$  are assigned to Ti-Cl vibrations. The band at  $390\text{cm}^{-1}$  is assigned to Ti-O vibrations and the strong band at  $760\text{cm}^{-1}$  is assigned to Ti-OPh-Ti bridge vibrations.

The  $^1\text{H}$  NMR spectrum of the compound has resonances at 7.25 p.p.m., 4.4 p.p.m., 2.07 p.p.m., and 1.25 p.p.m. The broad resonance at 7.25 p.p.m., is due to the protons of the phenoxide group. The resonances at 4.4 p.p.m.,



and 2.07 p.p.m. are due to coordinated tetrahydrofuran and the resonance at 1.25 p.p.m. is due to the methyl protons of the carboxylate. The integrals show the ligands are present in the ratio  $1 \text{ C}_6\text{H}_5\text{O}^- : 2\text{THF} : 2(\text{CH}_3)_3\text{CCO}_2^-$ .

Reaction of phenol, THF and  $\text{TiCl}_3(\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$  produces an orange solid. The  $^1\text{H}$  NMR spectrum of this solid contains resonances due to  $\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2^-$  (8.05 p.p.m., 7.9 p.p.m., 7.35 p.p.m., and 2.45 p.p.m.) and THF (4.75 p.p.m., 2.24 p.p.m.). No resonances due to  $\text{C}_6\text{H}_5\text{O}^-$  were observed. It is difficult to detect the presence of phenoxide groups from the infra-red spectrum. Bands at  $1510\text{cm}^{-1}$  and  $1415\text{cm}^{-1}$  are assigned to  $\nu(\text{CO}_2^-)_{\text{sym}}$  and  $\nu(\text{CO}_2^-)_{\text{asym}}$  respectively. The resulting  $\Delta$  value of  $95\text{cm}^{-1}$  according to the Deacon and Phillips criteria<sup>(57)</sup> indicates the presence of chelating or both bridging and chelating carboxylate groups. The elemental analysis of the complex is inconclusive but from the spectral evidence it appears the complex is probably  $[\text{TiCl}_2(\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2)\text{THF}]_2\text{O}$ .

Similarly reaction of  $\text{TiCl}_3(\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$ , THF and  $\text{C}_6\text{H}_2\text{Cl}_3\text{OH}$  produces an orange solid which analyses as  $[\text{TiCl}_2(\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2)\text{THF}]_2\text{O}$ . The  $^1\text{H}$  NMR spectrum contains resonances at 8.05 p.p.m., 7.9 p.p.m., 7.35 p.p.m., 2.45 p.p.m., (due to  $\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2^-$ ) and 4.8 p.p.m. and 2.25 p.p.m., (due to THF). No resonances due to  $\text{C}_6\text{H}_2\text{Cl}_3\text{O}^-$  were observed.

As before it proved difficult to detect the presence of  $\text{C}_6\text{H}_2\text{Cl}_3\text{O}^-$  from the infra-red spectrum of the product. Bands at  $1510\text{cm}^{-1}$  and  $1415\text{cm}^{-1}$  are assigned to  $\nu(\text{CO}_2^-)_{\text{asym}}$  and  $\nu(\text{CO}_2^-)_{\text{sym}}$  respectively. The resulting  $\Delta$  value of  $95\text{cm}^{-1}$  may indicate the presence of either chelating or bridging and chelating carboxylates<sup>(57)</sup>.

**(iii) Reaction of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with resorcinol (1,3 - dihydroxybenzene.)**

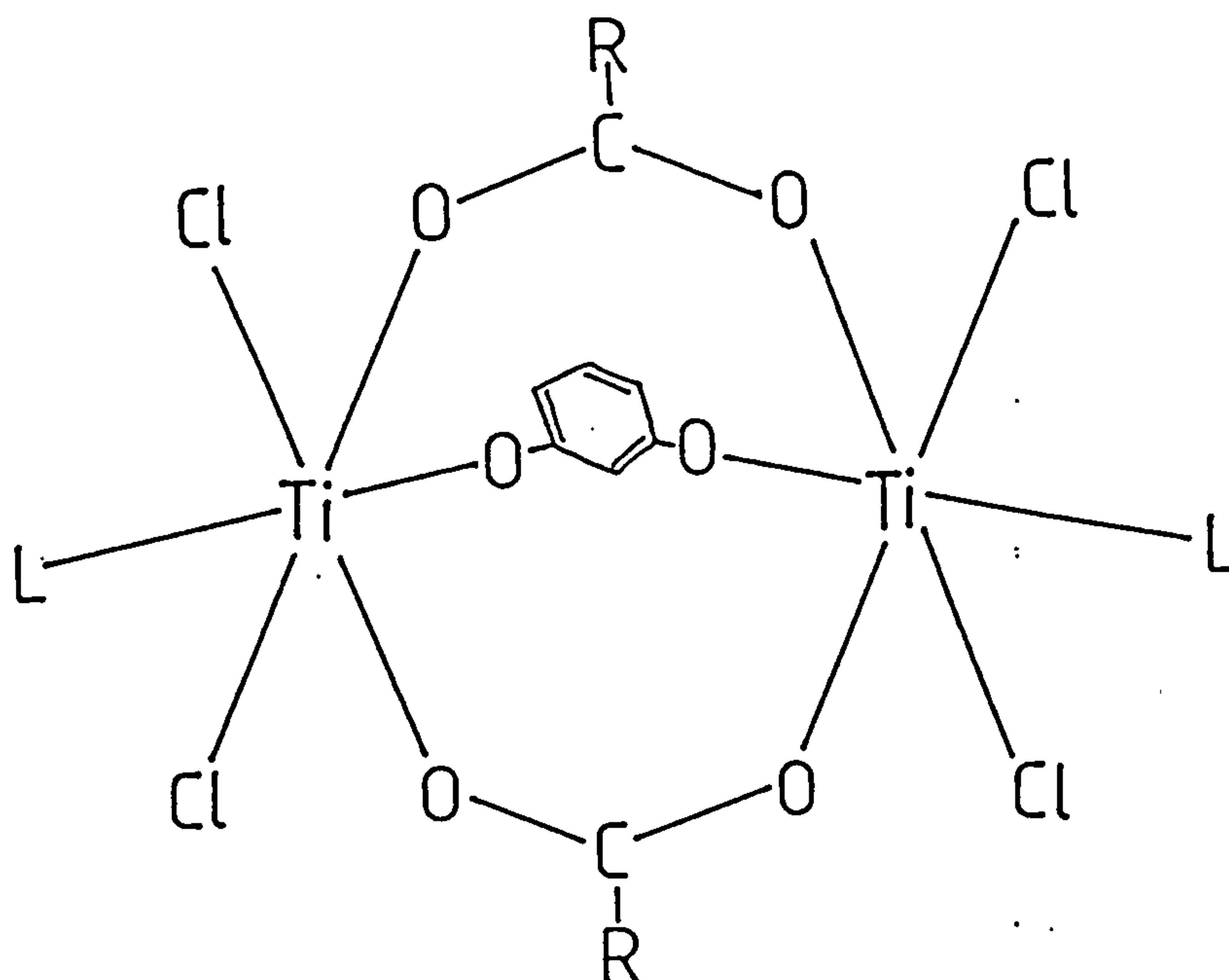
Resorcinol ( $\text{C}_6\text{H}_4(\text{OH})_2$ ) has two removeable hydrogen atoms and so may form chelated or bridged species with metals. Resorcinol was reacted with  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  in ethyl acetate solution to form a dark red solid.

The  $^1\text{H}$  NMR spectrum of the solid has signals due to  $(\text{CH}_3)_3\text{CCO}_2^-$  (1.1 - 1.5 p.p.m.), EtOAc (4.25, 2.25, 1.2 p.p.m) and  $\text{C}_6\text{H}_4\text{O}_2^-$  (6.6 - 7.5 p.p.m.) in the ration 2:2:1.

The infra-red spectrum contains bands at  $1650\text{cm}^{-1}$  and  $1540\text{cm}^{-1}$  in the carboxylate stretching region. These bands are assigned to  $\nu(\text{CO}_2^-)_{\text{asym}}$  and  $\nu(\text{CO}_2^-)_{\text{sym}}$  respectively. The  $\Delta$  value is  $110\text{cm}^{-1}$  which may indicate the presence of bridging and/or chelating carboxylate groups(57).

The elemental analysis of the solid agrees with the formulation  $\{\text{TiCl}_2[(\text{CH}_3)_3\text{CO}_2]\text{EtOAc}\}_2\text{O}_2\text{C}_6\text{H}_4$ . A possible structure for this complex is shown overleaf:





#### (iv) Reaction of $\text{TiCl}_3(\text{RCO}_2)$ with acetylacetone

Acetylacetone (Hacac) is a very effective chelating ligand. It was decided to attempt the preparation of mixed acetylacetonate, carboxylate complexes in order to determine the effect of the chelating ligand upon the properties of the carboxylate.

Stirring  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with Hacac in benzene for 15 hours produces an orange solid which from analytical evidence appears to be  $\text{TiCl}_2(\text{CH}_3\text{COCHCOCH}_3)[(\text{CH}_3)_3\text{CCO}_2]$ .

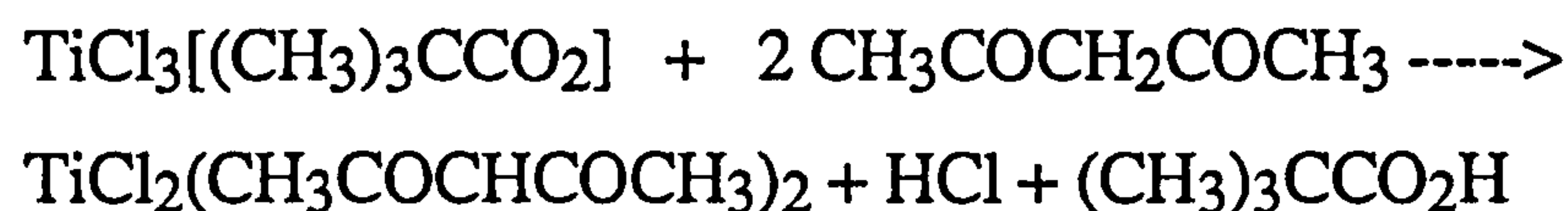
The infra-red spectrum of the product contains a number of bands in the carbonyl stretching region. A band at  $1670\text{cm}^{-1}$  is assigned as  $\nu(\text{CO}_2)_{\text{asym}}$  for the carboxylate ligand. Bands at  $1420\text{cm}^{-1}$  and  $1320\text{cm}^{-1}$  are assigned to  $\text{CH}_3$  vibrations, a band at  $1530\text{cm}^{-1}$  is assigned as  $\nu(\text{C O}) + \nu(\text{C C})$  for the acac ligand.

The  $^1\text{H}$  NMR spectrum of the compound has resonances at 6.0 p.p.m., 2.2 p.p.m. and 1.1 - 1.5 p.p.m. These are in the ratio 1:6:9. The resonance at 6 p.p.m. is assigned to the CH of acac, the resonance at 2.2 p.p.m. to the

methyl protons of acac and the resonance at 1.1 -1.5 p.p.m. to the methyl protons of  $(\text{CH}_3)_3\text{CCO}_2^-$ . The  $^1\text{H}$  NMR spectrum indicates the presence of equal numbers of pivalate and acac ligands.

The orange solid was recrystallised and an X-ray single crystal structure determination attempted. The structure proved impossible to fully solve although the partial solution obtained showed that the complex had changed upon recrystallisation. The carboxylate ligands had been almost completely displaced and a titanium (IV) acetylacetonate species had formed.

Reacting  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with two equivalents of Hacac produced a red powder. Comparison of the infra-red and  $^1\text{H}$  NMR spectra of the powder to those of  $\text{TiCl}_2(\text{acac})_2$  showed the powder to be  $\text{TiCl}_2(\text{acac})_2$ .  $\text{TiCl}_2(\text{acac})_2$  was prepared as described by Fay and Lowry<sup>(86)</sup>. Titanium tetrachloride was reacted with a  $\text{CH}_2\text{Cl}_2$  solution of Hacac, hexane being used to precipitate the red product. Equations for the two reactions producing  $\text{TiCl}_2(\text{acac})_2$  are shown below:



In general the reaction of  $\text{TiCl}_3(\text{RCO}_2)$  ( $\text{R} = \text{C}_6\text{H}_5, o\text{-CH}_3\text{C}_6\text{H}_4$ ) with Hacac produced a mixture of  $\text{TiCl}_2(\text{acac})_2$  and the parent carboxylic acid. The displacement of the carboxylate occurs very quickly, in the case of the benzoate being complete after ten minutes.

$\text{TiCl}_2(\text{acac})_2$  will not react with carboxylic acids even after heating in benzene for over 48 hours. A mixture of the bis-acetylacetonate and carboxylic acid is obtained from the reaction vessel. The carboxylic acid may be recovered unchanged by washing with hexane.

These reactions are summarised in Table 2.5.

The formation of  $\text{TiCl}_2(\text{acac})_2$  rather than mixed acetylacetonate/carboxylate compounds is probably promoted by the chelate effect. Mixed  $\text{RCO}_2\text{-acac}$  complexes would probably be oligomers but  $\text{TiCl}_2(\text{acac})_2$  is a monomer. Therefore the formation of monomeric  $\text{TiCl}_2(\text{acac})_2$  from oligomeric  $\text{TiCl}_3(\text{RCO}_2)$  species increases entropy. Using the thermodynamic relationships:

$$\Delta G^\circ = -RT \ln \beta$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

( $\beta$  = equilibrium constant)

It can be seen that the increase in entropy will cause  $\Delta G^\circ$  to become more negative, increasing  $\log \beta$  and favouring the formation of  $\text{TiCl}_2(\text{acac})_2$  over mixed  $\text{acac/RCO}_2\text{-}$  complexes.

#### (v) Reactions of $\text{TiCl}_3(\text{RCO}_2)$ with dibenzoylmethane

Dibenzoylmethane ( $\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$ ) is a chelating ligand similar to acetylacetone. The two phenyl rings make it considerably more bulky than acetylacetone.



Table 2.5 : Reactions of  $\text{TiCl}_3(\text{RCO}_2)$  species with acetylacetone.

Starting Materials	Reaction Time	Result
$\text{TiCl}_3(\text{Me}_3\text{CCO}_2)$ + acac	15h	$\text{TiCl}_3(\text{acac})(\text{Me}_3\text{CCO}_2)$ changes form on recrystallization
$\text{TiCl}_2(\text{acac})_2$ + $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ in $\text{C}_6\text{H}_6$	reflux 48h	mixture of benzoic acid and $\text{TiCl}_2(\text{acac})_2$
$\text{TiCl}_2(\text{acac})_2$ + $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ in $\text{CH}_2\text{Cl}_2$	reflux 3h	mixture of benzoic acid and $\text{TiCl}_2(\text{acac})_2$
$\text{TiCl}_3(\text{Me}_3\text{CCO}_2)$ + $2\text{Hacac}$ in $\text{C}_6\text{H}_6$	1/2h	$\text{TiCl}_2(\text{acac})_2$
$\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$ + $\text{Hacac}$ in $\text{C}_6\text{H}_6$	15h	$\text{TiCl}_2(\text{acac})_2$ + benzoic acid
$\text{TiCl}_3(o\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$ + $\text{Hacac}$ in toluene	36h	$\text{TiCl}_2(\text{acac})_2$ + $o\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2\text{H}$
$\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$ + $\text{Hacac}$ in benzene	10 minutes	$\text{TiCl}_2(\text{acac})_2$ + benzoic acid



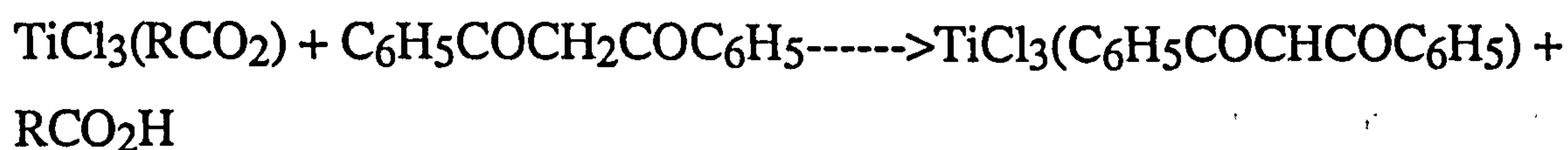
The reactions of  $\text{TiCl}_3(\text{RCO}_2)$   $\text{R} = (\text{CH}_3)_3\text{C}$ ,  $\text{o-CH}_3\text{C}_6\text{H}_4$  and  $\text{C}_6\text{H}_5$  with dibenzoylmethane produce a red powder. The infra-red spectra of the red powders produced using different carboxylates were identical. This indicates that the same product is formed whatever carboxylate is reacted with dibenzoylmethane.

Bands at  $1600\text{cm}^{-1}$  and  $1585\text{cm}^{-1}$  are assigned to aromatic ring vibrations. A band at  $1530\text{cm}^{-1}$  is assigned to  $\nu(\text{C}\equiv\text{O}) + \nu(\text{C}\equiv\text{C})$  of dibenzoylmethane.

No resonances due to carboxylate ligands are seen in the  $^1\text{H}$  NMR of the product. Resonances are observed at 8.1 p.p.m., 7.5 p.p.m. (due to  $\text{C}_6\text{H}_5$  protons) and 1.25 p.p.m. (due to CH protons).

Comparison of the F.A.B. mass spectra of the complexes to those of a genuine sample of  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)$  showed the products were all  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)$ . The  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)$  was prepared by the reaction of titanium tetrachloride and dibenzoylmethane in dichloromethane solution.

The dibenzoylmethane displaces the carboxylate ligand forming the complex and the free acid. The displacement apparently occurs since the chelate effect makes the dibenzoylmethane complex energetically favourable compared to the carboxylate. The bis-complex is probably not formed as the dibenzoylmethane ligand is too sterically hindering to allow its facile formation.



**(iv) Reaction of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with triphenylphosphine**

The reaction of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with triphenylphosphine in dichloromethane solution produced a brown solid. Recrystallisation isolated blue, brown and orange solids and a green solution. The  $^1\text{H}$  NMR spectra of all the solids contained broad resonances due to the  $\text{Ph}_3\text{P}$  group. The solids proved to be inhomogeneous and attempts both to purify and analyse them proved unsuccessful.

**(vii) Reaction of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with pyridine**

The 1:1 reaction of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  and pyridine produces a yellow solid. This solid is only soluble in pyridine. The infra-red spectrum of the solid contains bands at  $1640\text{cm}^{-1}$  and  $1485\text{cm}^{-1}$  due to  $\nu(\text{CO}_2)_{\text{asym}}$  and  $\nu(\text{CO}_2)_{\text{sym}}$  respectively. A band at  $240\text{cm}^{-1}$  is assigned as a Ti-py vibration and a band at  $350\text{cm}^{-1}$  is assigned as a Ti-Cl vibration. The band at  $650\text{cm}^{-1}$  is assigned to pyridine in-plane ring deformations; it occurs at  $604\text{cm}^{-1}$  in free pyridine<sup>(56)</sup>. The band at  $440\text{cm}^{-1}$  is assigned to pyridine out-of-plane ring deformation; it occurs at  $405\text{cm}^{-1}$  in free pyridine<sup>(56)</sup>. The bands due to pyridine are in general stronger than those due to the carboxylate in the infra-red spectrum.

The 2:1 reaction of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  and pyridine produces a yellow solid. This solid is soluble in boiling  $\text{CH}_3\text{CN}$  and in pyridine. No bands due to carboxylate were observed in the infra-red spectrum of the solid. A band at  $370\text{cm}^{-1}$  is assigned to Ti-Cl vibrations.

It appears that in both 1:1 and 1:2 reactions of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with pyridine that the carboxylate is displaced and an insoluble pyridine complex formed. The product from the 1:1 reaction still contained some carboxylate however.

This result is interesting as Kapoor and coworkers claim to have prepared the  $\text{TiCl}_3(\text{CH}_3\text{CO}_2) \cdot 2\text{py}$  adduct and the  $\text{TiCl}_3(\text{RCO}_2) \cdot \text{py}$  adducts where  $\text{R} = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$  and  $\text{C}_5\text{H}_{11}$ .<sup>114</sup> The behavior of the titanium (IV) pivalate with pyridine appears to be different to that of the carboxylates studied by Kapoor.

### Infra-red Spectra of titanium (IV) carboxylates

Carboxylate stretching frequencies and  $\Delta$  values for a range of  $\text{TiCl}_3(\text{RCO}_2)$  species are shown in Table 2.6.

Most of the values are between  $120 - 160\text{cm}^{-1}$  indicating the presence of chelating and/or bridging carboxylates.  $\text{TiCl}_3(o\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$  has a  $\Delta$  value of  $210\text{cm}^{-1}$  and  $\text{TiCl}_3[\text{C}_6\text{H}_2(\text{CH}_3)_3\text{CO}_2]$  has a  $\Delta$  value of  $110\text{cm}^{-1}$ . This may be due to steric considerations as both derivatives have *ortho* methyl groups which may influence the  $\text{CO}_2^-$  group.



Table 2.6 : Infra-red Spectra of  $\text{TiCl}_3(\text{RCO}_2)$ .

Carboxylate	(CO <sub>2</sub> )asym (cm <sup>-1</sup> )	(CO <sub>2</sub> )sym (cm <sup>-1</sup> )	(cm <sup>-1</sup> )
$\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$	1555	1410	145
$\text{TiCl}_3[(\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{CCO}_2]$	1645	1530	115
$\text{TiCl}_3[(\text{CH}_3)_2\text{CHCO}_2]$	1650	1500	150
$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$	1643, 1553	1508, 1428	135, 125
$\text{TiCl}_3(\text{C}_9\text{H}_6\text{NCO}_2)$	1585	1428	157
$\text{TiCl}_3(o\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$	1550	1340	210
$\text{TiCl}_3(p\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$	1530	1410	120
$\text{TiCl}_3[\text{C}_6\text{H}_2(\text{CH}_3)_3\text{CO}_2]$	1595	1485	110
$\text{TiCl}_3(\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2)$	1545	1390	155
$\text{TiCl}_3(\text{CH}_3\text{CH}=\text{CHCO}_2)$	1580	1425	155



## CONCLUSIONS

Titanium (IV) carboxylates may be prepared by reaction of titanium tetrachloride with carboxylic acids in an organic solvent. Some carboxylates are difficult to prepare because of problems with solubility and side reactions. If there is a possibility of interaction between the titanium and the alkyl chain of the acid, reduction of the titanium may occur.

The reaction of titanium (IV) tris(chloro)monocarboxylates with strong donor ligands results in the displacement of the carboxylate ligand and formation of a complex. If the ligands are good chelating agents again the carboxylate will be displaced and a chelate complex formed.

The scrambling of the carboxylate ligands in solution involves the titanium - oxygen bonds breaking and reforming. This may make the titanium vulnerable to attack by other ligands. Once another ligand has bonded to the titanium the carboxylate is unable to displace it in order to reform the original complex.

The reactions with phenol and resorcinol show that an oxygen bridge is preferred in complexes of the type  $[\text{TiCl}_2(\text{RCO}_2)\text{L}]_2 \text{Bd}$  (where Bd is a bridging atom or molecule). However if no water is present alkoxy or dialkoxy bridges may be formed.

**CHAPTER 3**  
**STRUCTURE AND SPECTRAL**  
**PROPERTIES**  
**OF**  
**TiCl<sub>3</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>]**

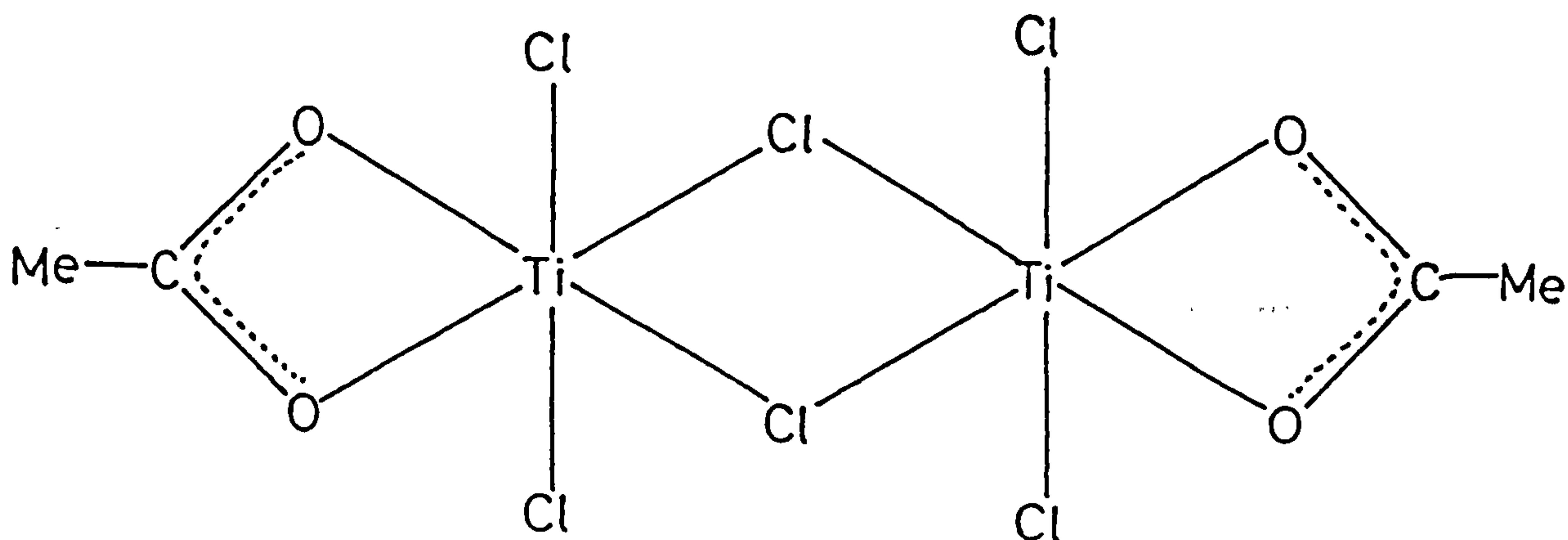
## Structure and Spectral Properties of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$

### Introduction

The molecular structure of titanium trischloromonocarboxylate species has not been previously established. Knowledge of the molecular structure would be useful in the explanation of the spectral and physical properties of such species. Therefore it was decided to perform a single crystal x-ray diffraction study on  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$ , and to use the result in the interpretation of the spectral and physical properties of this complex.

Crystals of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  suitable for examination by diffraction methods were very difficult to grow. The crystals were often twinned making them unusable. The crystals were mounted in thin glass tubes under argon. If the crystals were mounted under nitrogen they decomposed when exposed to the x-ray beam.

Amaudrut and coworkers performed infra-red and cryoscopic molecular mass studies upon  $\text{TiCl}_3(\text{CH}_3\text{CO}_2)$ (121) They assigned three bands in the infra-red spectrum to COO vibrations,  $1610\text{cm}^{-1}$ ,  $1490\text{cm}^{-1}$  and  $1395\text{cm}^{-1}$ . It was claimed that the complex was monomeric in dilute benzene solution and dimeric in concentrated benzene solution. From these measurements Amaudrut proposed the structure below:



The structure is linked by chlorine bridges and contains bidentate chelating carboxylates. The carboxylates will be strained in this configuration as the OCO angle will be forced to decrease. This will increase interactions between orbitals on the two oxygens thus inducing strain into the OCO unit.

### Studies on titanium(IV) bischlorobis(carboxylate) species

No single crystal X-ray diffraction studies of titanium (IV) bischlorobis(carboxylate) species have been performed. By comparison of the infrared spectra of the bis-bromo and bis-chloro carboxylates Amaudrut et al<sup>(115)</sup> claim that the halides in these species are *trans* to each other and that the titanium atoms have a  $\text{MO}_4\text{X}_2$  pseudo-octahedral co-ordination. Cryoscopic molecular mass measurements show the complexes are dimeric in benzene solution. Amaudrut suggested the structure shown in Figure 3.1 for  $\text{TiX}_2(\text{RCO}_2)_2$  complexes.

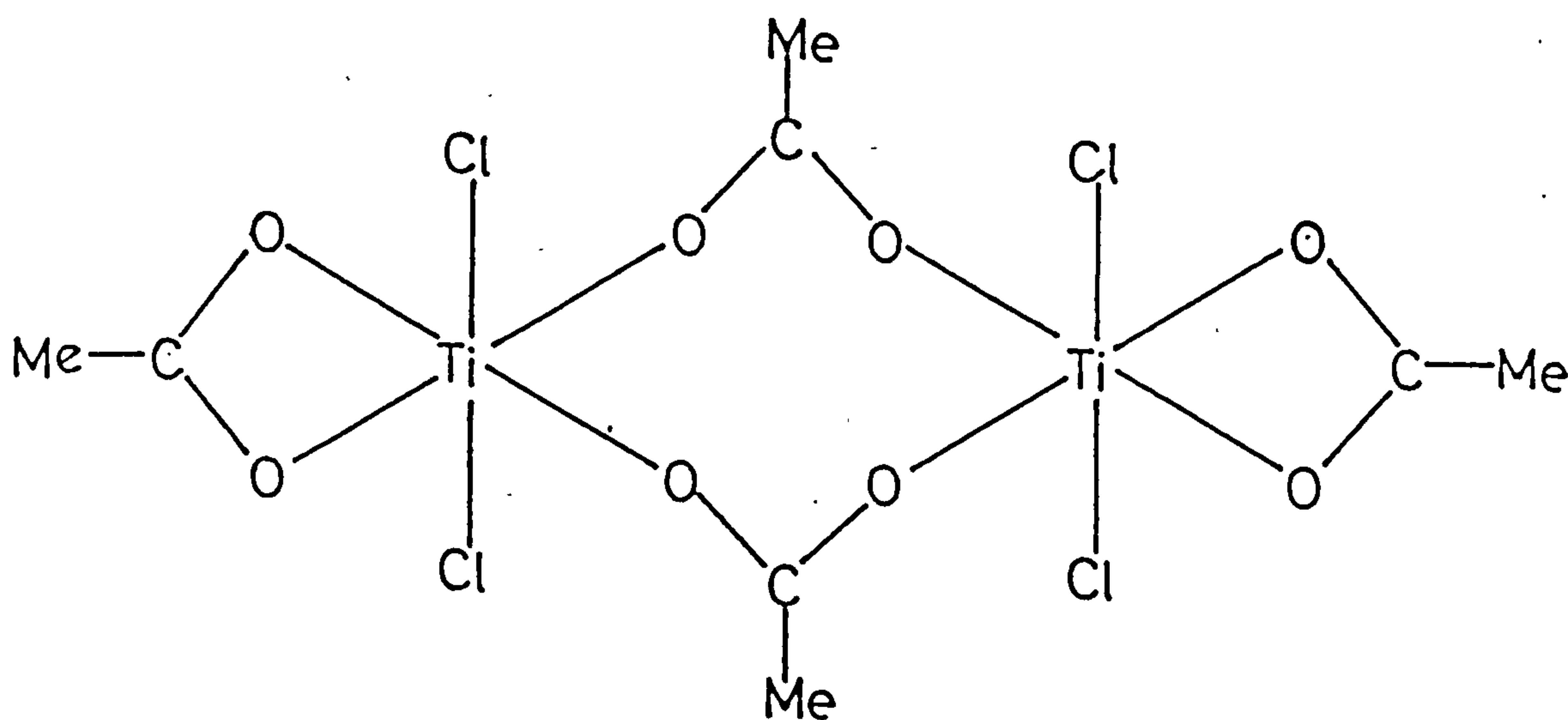


Figure 3.1: A possible structure for  $\text{TiX}_2(\text{RCO}_2)_2$  complexes.



## Solid state infra-red spectrum of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$

The infra-red spectrum and band assignments for  $\text{TiCl}_3[(\text{CH}_3)_3\text{CO}_2]$  are reported in Table 3.1. The assignments are tentative being based upon comparison with the free acid and related metal carboxylate species.

The most significant feature of the infra-red spectrum is the four bands due to  $\nu(\text{COO}^-)$ . These may be paired to give  $\Delta$  values. The band at  $1643\text{cm}^{-1}$  pairs with the one at  $1508\text{cm}^{-1}$  and the band at  $1553\text{cm}^{-1}$  pairs with the band at  $1428\text{cm}^{-1}$ .

Using the formula:

$$\Delta = \nu(\text{COO}^-)_{\text{asym}} - \nu(\text{COO}^-)_{\text{sym}}$$

gives  $\Delta$  values of  $135\text{cm}^{-1}$  and  $125\text{cm}^{-1}$  respectively. These values are consistent with the presence of chelating and/or bridging carboxylates<sup>(57)</sup>.

## $^1\text{H}$ NMR Spectrum of $\text{TiCl}_3[(\text{CH}_3)_3\text{CO}_2]$

The proton NMR spectrum of free pivalic acid contains two peaks, one at 12.0 p.p.m. due to the hydroxyl proton and one at 1.2 p.p.m. due to the nine equivalent protons of the tertiary butyl group.

In the spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (Figure 3.2) there is no peak at 12 p.p.m. and the singlet at 1.2 p.p.m. due to the tertiary butyl group has changed to a complex multiplet centred around 1.15 p.p.m. The multiplet contains at least nine peaks. The largest of these is at 1.16 p.p.m.

By comparison of the spectrum with those of petroleum ether (b.p. 60-80°C) and high vacuum grease it appears that the multiplet is not due to these impurities. It has to be pointed out that this compound did produce variable results in the  $^1\text{H}$  n.m.r. spectra recorded. The spectrum shown in Figure 3.2 is typical of the kind of spectrum obtained. The resonances of the protons of the alkyl group were often broad and unresolved when the spectrum was run in  $\text{CDCl}_3$  solution at 400 MHz. Although no satisfactory explanation can be offered for this behaviour, it was apparent that better defined spectra were obtained when the samples were made up using  $\text{C}_6\text{D}_5\text{CD}_3$  for the variable temperature spectra (Figure 3.3). The spectra are discussed further on page 111.

Table 3.1 Infra-red Spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$

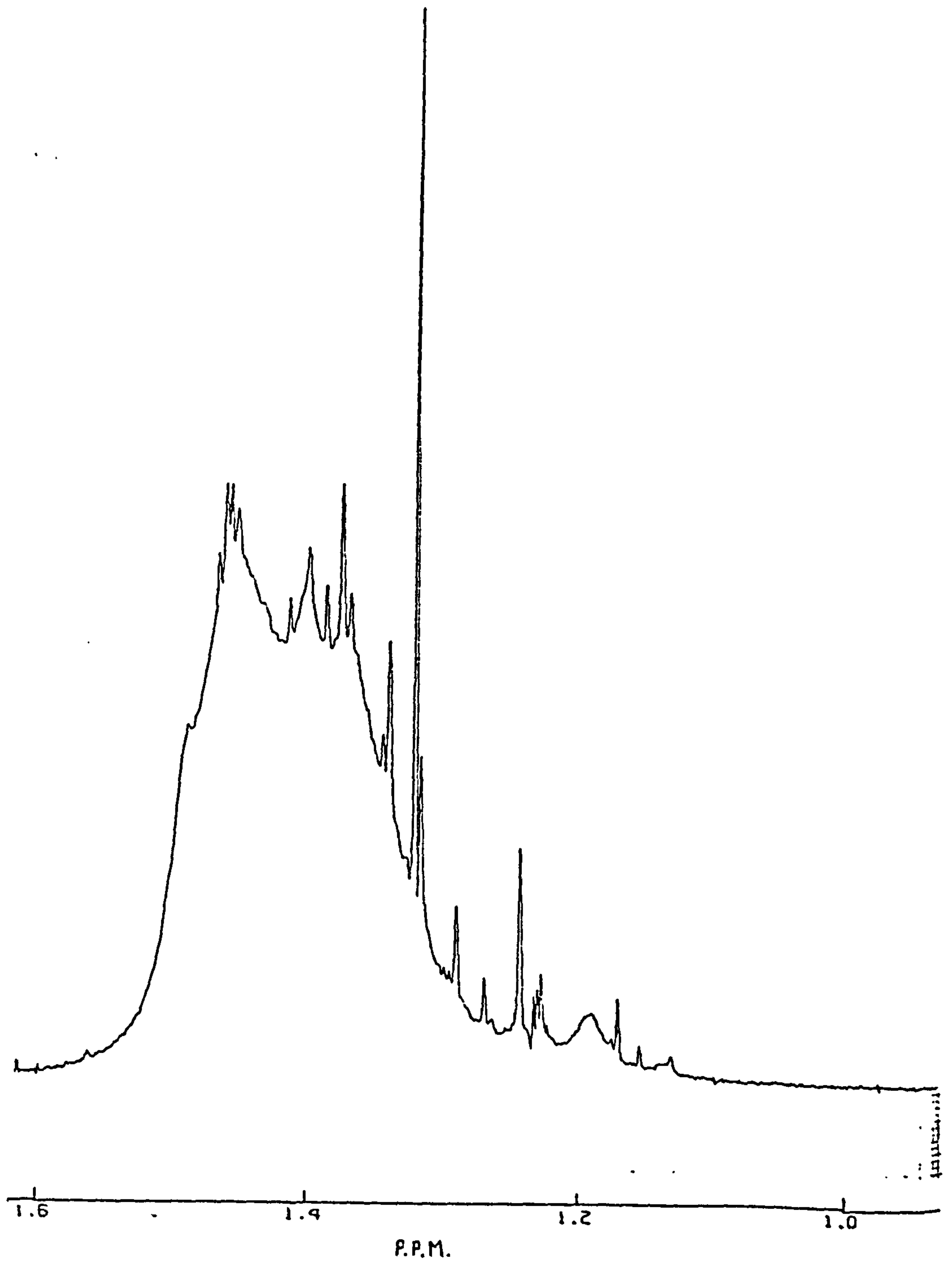
Bands occur at: (all in  $\text{cm}^{-1}$ )

1643, 1553, 1508(s), 1488(s), 1428(s), 1371(s), 1233(s), 1033, 938(w), 778(w), 613(s), 496, 458, 403(s), 323(sh).

Assignments:

1643 $\text{cm}^{-1}$	=	$\nu(\text{COO}^-)_{\text{asym}}$
1553 $\text{cm}^{-1}$	=	$\nu(\text{COO}^-)_{\text{asym}}$
1508 $\text{cm}^{-1}$	=	$\nu(\text{COO}^-)_{\text{sym}}$
1488 $\text{cm}^{-1}$	=	C-H deformations
1428 $\text{cm}^{-1}$	=	$\nu(\text{COO}^-)_{\text{sym}}$
1371 $\text{cm}^{-1}$	=	due to $\text{C}(\text{CH}_3)_3$ vibrations
1233 $\text{cm}^{-1}$	=	C-O stretching
613 $\text{cm}^{-1}$	=	O-C=O bending
496 $\text{cm}^{-1}$	=	O-C = O in plane bending
403 $\text{cm}^{-1}$	=	terminal Ti-Cl stretching

Figure 3.2: The  $^1\text{H}$  NMR Spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$





## Variable temperature $^1\text{H}$ NMR of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$

In order to investigate the multiple peak in the  $^1\text{H}$  NMR spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  the  $^1\text{H}$  NMR spectrum of the complex was obtained at various different temperatures. The temperatures ranged from 253K to 373K. The spectra are shown in Figure 3.3.

At 253K the individual peaks may be clearly distinguished, in three main groupings centred around 1.1 p.p.m., 1.25 p.p.m. and 1.36 p.p.m. The peak at 1.36 p.p.m. broadens as the temperature is increased and the peaks at 1.1, 1.25 p.p.m. disappear. The sharp peak around 1.15 p.p.m. grows in intensity.

The rise in temperature causes all of the peaks to shift downfield slightly. For example an increase in temperature from 293K to 373K causes peak (A) to move from 1.15 to 1.22 p.p.m.

In the spectrum run at 373K peaks (B), (C) and (D) have almost coalesced. It is expected at higher temperatures that the spectrum would consist of only two peaks, one around 1.4 p.p.m. and the other around 1.25 p.p.m. The integrals show 4.5 - 5.0 times more protons are responsible for the broad peaks at 1.4 p.p.m. than for the sharp peak at 1.22 p.p.m.

## $^1\text{H}$ NMR decoupling experiments.

It is possible that the multiple peak in the  $^1\text{H}$  NMR spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  is caused by proton spin-spin coupling. If it is then irradiation at the frequency of one peak will decouple it from the others and should simplify the spectrum.

No changes in the spectrum were observed when the peaks were decoupled. Therefore the multiple peaks do not arise from proton spin-spin coupling.

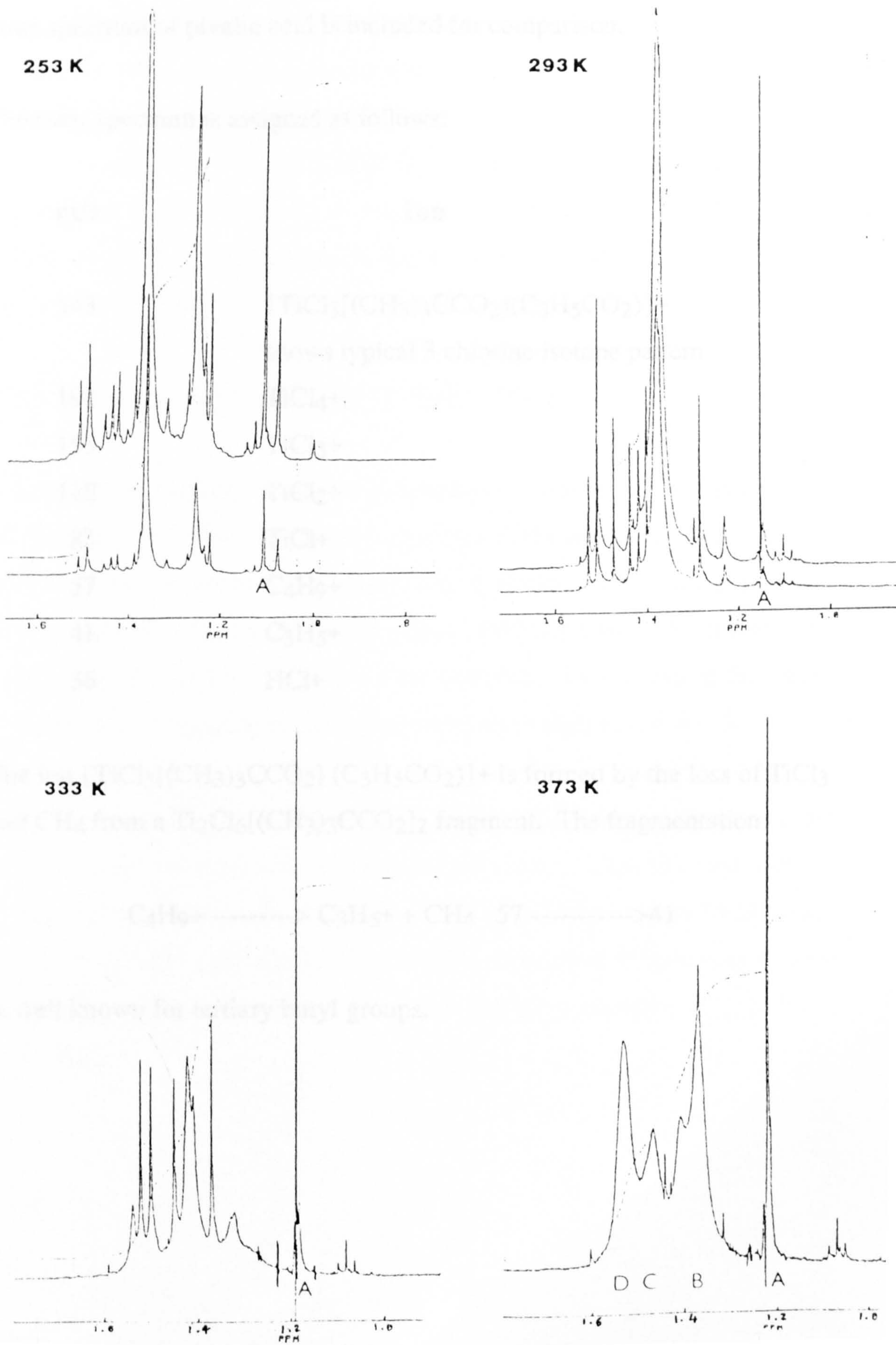
### **$^{13}\text{C}$ NMR of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$**

The proton decoupled  $^{13}\text{C}$  spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  contains three resonances:

189.58 p.p.m.	$\text{CO}_2^-$ group
128.16 p.p.m.	tertiary carbon
26.71 p.p.m.	methyl carbons

In the  $^{13}\text{C}$  spectrum of free pivalic acid the carboxyl resonance occurs at 185 p.p.m. The observed 4.58 p.p.m. shift (to 189.58 p.p.m.) in the spectrum of the complex indicates formation of the carboxylate anion. The other resonances occur at similar frequencies to those of the free acid.

Figure 3.3: Variable temperature  $^1\text{H}$  NMR spectra of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$





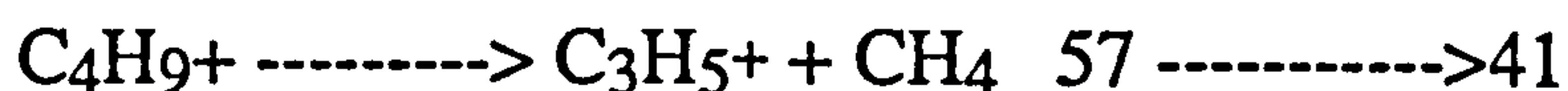
## Electron impact mass spectrum of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$

The mass spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  is reported in Table 3.2. The mass spectrum of pivalic acid is included for comparison.

The mass spectrum is assigned as follows:

m/z	Ion
343	$\{\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2](\text{C}_3\text{H}_5\text{CO}_2)\}^+$ shows typical 3 chlorine isotope pattern
190	$\text{TiCl}_4^+$
153	$\text{TiCl}_3^+$
118	$\text{TiCl}_2^+$
83	$\text{TiCl}^+$
57	$\text{C}_4\text{H}_9^+$
41	$\text{C}_3\text{H}_5^+$
36	$\text{HCl}^+$

The ion  $\{\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2](\text{C}_3\text{H}_5\text{CO}_2)\}^+$  is formed by the loss of  $\text{TiCl}_3$  and  $\text{CH}_4$  from a  $\text{Ti}_2\text{Cl}_6[(\text{CH}_3)_3\text{CCO}_2]_2$  fragment. The fragmentation



is well known for tertiary butyl groups.



## Cryoscopic molecular weight measurements on $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$

Cryoscopic molecular weight measurements indicate  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  molecules exist as dimeric units in benzene solution. The complex remains dimeric at both high and low concentrations. This behavior is different to that reported for  $\text{TiCl}_3(\text{CH}_3\text{CO}_2)$  which is monomeric at low concentrations and dimeric at high concentrations<sup>(121)</sup>. In view of the importance of this measurement it was repeated several times, and the same result was obtained each time.

## Molecular structure of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$

A single crystal x-ray structure determination upon  $\text{TiCl}_3[(\text{CH}_3)_3\text{CO}_2]$  revealed that the compound exists as a trimer in the solid state. The titanium atoms form an approximate isosceles triangle. They are joined by carboxylate ligands and chlorine bridges. Tables 3.3 and 3.5 contain bond lengths and angles respectively for the complex. Two views of the trimer and the atom numbering scheme are presented in Figures 3.4 and 3.5.

An interesting feature of the structure is the triply bridging chlorine atom (Cl(3)) which connects the three titanium atoms. This chlorine atom is located 0.961 Å above the  $\text{Ti}_3$  plane. Its bond to Ti(3) is long (2.839 Å) and its bonds to Ti(1) and Ti(2) (2.577, 2.565 Å) show some lengthening relative to the titanium-chlorine bonds of the bridging chlorine Cl(2) (2.49, 2.476 Å).

**Table 3.2                    Mass Spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$**

m/z value	339	341	343	345	194	192	190	188	157
Relative abundance	223	412	398	233	46	180	351	279	543
m/z	155	153	122	120	118	85	83	57	41
R.A.	691	702	120	490	588	199	800	1000	684
m/z	36								
R.A.	247								

**Mass Spectrum of  $(\text{CH}_3)_3\text{CCOOH}$**

m/z value	57	56	45	41	39	29	28	27	18	17
Relative Abundance	1000	64	85	420	132	308	96	104	296	70

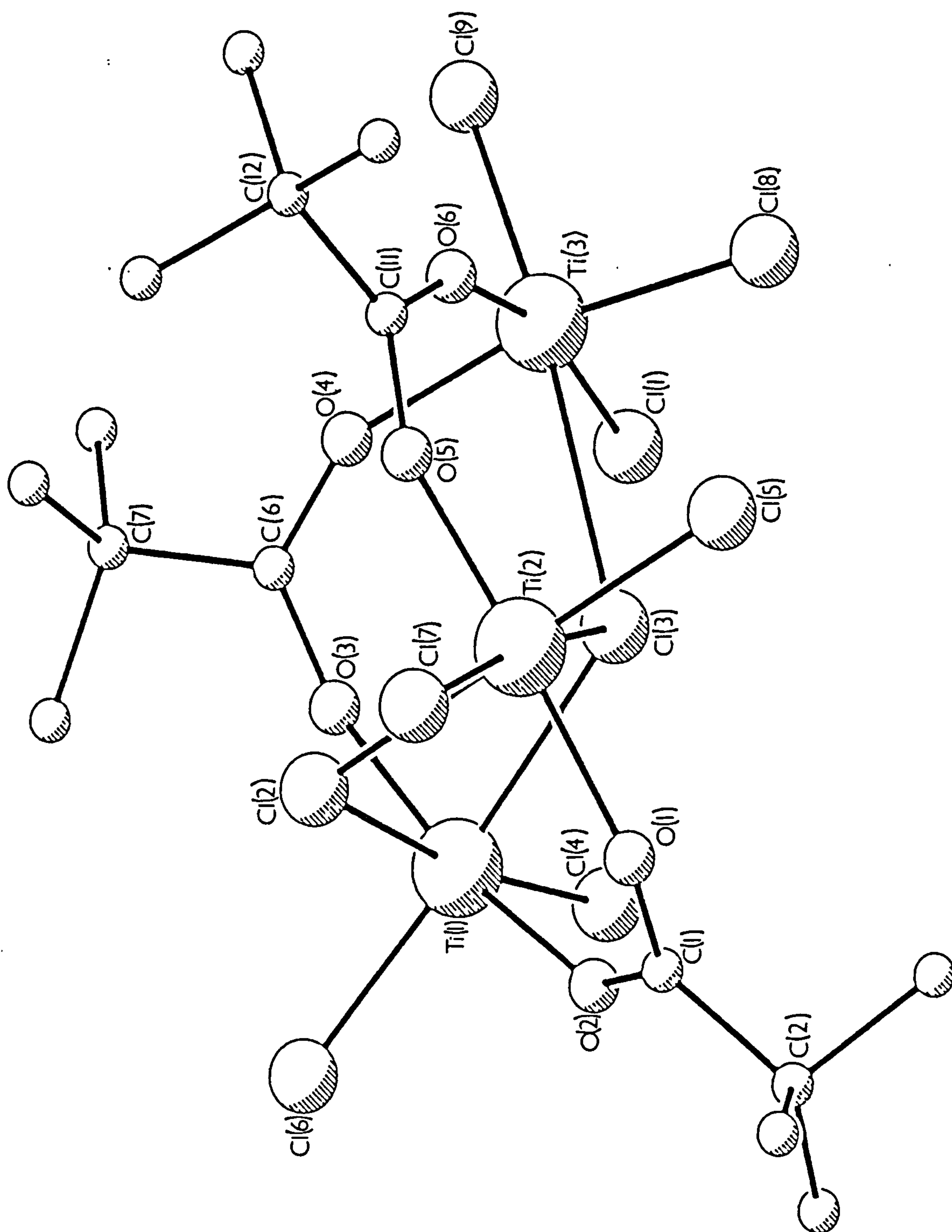


Figure 3.4: The structure of  $\text{Ti}_3\text{Cl}_9[(\text{CH}_3)_3\text{CCO}_2]_3$



Table 3.3: Bond lengths (Å)

Ti(1)-O1(2)	2.450(2)	Ti(1)-O1(3)	2.565(2)
Ti(1)-O1(4)	2.184(3)	Ti(1)-O1(6)	2.197(2)
Ti(1)-O(2)	1.953(4)	Ti(1)-O(3)	1.884(5)
Ti(2)-O1(2)	2.476(2)	Ti(2)-O1(3)	2.577(2)
Ti(2)-O1(5)	2.194(2)	Ti(2)-O1(7)	2.197(2)
Ti(2)-O(1)	1.965(5)	Ti(2)-O(5)	1.877(5)
Ti(3)-O1(1)	2.207(3)	Ti(3)-O1(3)	2.839(2)
Ti(3)-O1(8)	2.207(2)	Ti(3)-O1(9)	2.186(3)
Ti(3)-O(4)	1.985(5)	Ti(3)-O(6)	1.986(6)
O(1)-O(1)	1.261(10)	O(2)-O(1)	1.265(8)
O(3)-O(6)	1.253(9)	O(4)-O(6)	1.277(9)
O(5)-O(11)	1.269(8)	O(6)-O(11)	1.235(9)
O(1)-O(2)	1.503(11)	O(2)-O(31)	1.583(13)
O(2)-O(41)	1.553(13)	O(2)-O(51)	1.489(30)
O(2)-O(32)	1.612(57)	O(2)-O(42)	1.607(54)
O(3)-O(52)	1.422(37)	O(31)-O(52)	0.818(45)
O(41)-O(32)	1.548(63)	O(51)-O(32)	1.392(59)
O(51)-O(42)	0.988(53)	O(42)-O(52)	1.563(70)
O(6)-O(7)	1.514(9)	O(7)-O(81)	1.484(18)
O(7)-O(91)	1.567(17)	O(7)-O(101)	1.527(15)
O(7)-O(82)	1.340(54)	O(7)-O(92)	1.529(47)
O(7)-O(102)	1.643(38)	O(81)-O(92)	0.637(50)
O(91)-O(82)	0.956(49)	O(101)-O(82)	1.707(54)
O(101)-O(102)	0.806(46)	O(11)-O(12)	1.497(12)
O(12)-O(13)	1.537(13)	O(12)-O(14)	1.534(12)
O(12)-O(15)	1.566(12)	O(16)-O(18)	1.383(18)
O(16)-O(17a)	1.324(18)	O(17)-O(18)	1.378(18)
O(17)-O(16a)	1.324(18)		



Table 3.4: Bond angles (deg)

C1(2)-Ti(1)-C1(3)	78.8(1)	C1(2)-Ti(1)-C1(4)	170.7(1)
C1(3)-Ti(1)-C1(4)	91.9(1)	C1(2)-Ti(1)-C1(6)	88.6(1)
C1(3)-Ti(1)-C1(6)	166.7(1)	C1(4)-Ti(1)-C1(6)	100.6(1)
C1(2)-Ti(1)-O(2)	85.0(2)	C1(3)-Ti(1)-O(2)	90.6(1)
C1(4)-Ti(1)-O(2)	93.5(2)	C1(6)-Ti(1)-O(2)	94.0(1)
C1(2)-Ti(1)-O(3)	85.2(2)	C1(3)-Ti(1)-O(3)	85.7(1)
C1(4)-Ti(1)-O(3)	94.2(2)	C1(6)-Ti(1)-O(3)	97.7(1)
O(2)-Ti(1)-O(3)	164.5(2)	C1(2)-Ti(2)-C1(3)	78.8(1)
C1(2)-Ti(2)-C1(5)	167.9(1)	C1(3)-Ti(2)-C1(5)	89.1(1)
C1(2)-Ti(2)-C1(7)	90.8(1)	C1(3)-Ti(2)-C1(7)	168.7(1)
C1(5)-Ti(2)-C1(7)	101.3(1)	C1(2)-Ti(2)-O(1)	84.7(1)
C1(3)-Ti(2)-O(1)	80.8(1)	C1(5)-Ti(2)-O(1)	93.8(2)
C1(7)-Ti(2)-O(1)	94.0(2)	C1(2)-Ti(2)-O(5)	85.8(2)
C1(3)-Ti(2)-O(5)	87.1(2)	C1(5)-Ti(2)-O(5)	93.4(2)
C1(7)-Ti(2)-O(5)	96.5(2)	O(1)-Ti(2)-O(5)	165.9(2)
C1(1)-Ti(3)-C1(3)	83.2(1)	C1(1)-Ti(3)-C1(8)	97.3(1)
C1(3)-Ti(3)-C1(8)	83.3(1)	C1(1)-Ti(3)-C1(9)	99.0(1)
C1(3)-Ti(3)-C1(9)	174.6(1)	C1(8)-Ti(3)-C1(9)	101.3(1)
C1(1)-Ti(3)-O(4)	89.2(2)	C1(3)-Ti(3)-O(4)	79.0(2)
C1(8)-Ti(3)-O(4)	160.3(2)	C1(9)-Ti(3)-O(4)	96.1(2)
C1(1)-Ti(3)-O(6)	163.6(2)	C1(3)-Ti(3)-O(6)	82.2(2)
C1(8)-Ti(3)-O(6)	98.4(2)	C1(9)-Ti(3)-O(6)	94.9(2)
O(4)-Ti(3)-O(6)	80.7(2)	Ti(1)-C1(2)-Ti(2)	99.2(1)
Ti(1)-C1(3)-Ti(2)	94.7(1)	Ti(1)-C1(3)-Ti(3)	114.3(1)
Ti(2)-C1(3)-Ti(3)	113.5(1)	Ti(2)-O(1)-O(1)	141.5(4)
Ti(1)-O(2)-O(1)	141.9(5)	Ti(1)-O(3)-O(6)	151.6(5)
Ti(3)-O(4)-O(6)	150.5(5)	Ti(2)-O(5)-O(11)	153.4(5)
Ti(3)-O(6)-O(11)	153.8(5)	O(1)-O(1)-O(2)	122.5(6)
O(1)-O(1)-O(2)	118.0(6)	O(2)-O(1)-O(2)	119.5(7)
O(1)-O(2)-O(31)	108.2(8)	O(1)-O(2)-O(41)	105.0(7)
O(31)-O(2)-O(41)	100.5(8)	O(1)-O(2)-O(51)	112.1(11)
O(31)-O(2)-O(51)	121.4(12)	O(41)-O(2)-O(51)	107.8(12)
O(1)-O(2)-O(32)	105.0(20)	O(31)-O(2)-O(32)	144.6(19)
O(41)-O(2)-O(32)	58.6(21)	O(51)-O(2)-O(32)	53.2(23)
O(1)-O(2)-O(42)	105.3(18)	O(31)-O(2)-O(42)	92.6(19)
O(41)-O(2)-O(42)	141.0(21)	O(51)-O(2)-O(42)	37.0(21)
O(32)-O(2)-O(42)	90.1(29)	O(1)-O(2)-O(52)	111.3(18)
O(31)-O(2)-O(52)	31.0(18)	O(41)-O(2)-O(52)	126.2(17)
O(51)-O(2)-O(52)	93.9(21)	O(32)-O(2)-O(52)	138.5(29)
O(42)-O(2)-O(52)	61.8(25)	O(2)-O(31)-O(52)	63.5(26)
O(2)-O(41)-O(32)	62.6(20)	O(2)-O(51)-O(32)	68.0(29)
O(2)-O(51)-O(42)	78.0(38)	O(32)-O(51)-O(42)	146.0(50)
O(2)-O(32)-O(41)	58.8(32)	O(2)-O(32)-O(51)	58.9(23)
O(41)-O(32)-O(51)	113.3(37)	O(2)-O(42)-O(51)	65.0(32)
O(2)-O(42)-O(52)	53.3(23)	O(51)-O(42)-O(52)	111.0(45)
O(2)-O(52)-O(31)	85.5(29)	O(2)-O(52)-O(42)	64.9(24)
O(31)-O(52)-O(42)	149.7(41)	O(3)-O(6)-O(4)	121.7(6)
O(3)-O(6)-O(7)	120.9(6)	O(4)-O(6)-O(7)	117.4(7)
O(6)-O(7)-O(81)	108.1(7)	O(6)-O(7)-O(91)	107.3(7)
O(81)-O(7)-O(91)	111.8(9)	O(6)-O(7)-O(101)	108.0(7)
O(81)-O(7)-O(101)	112.1(10)	O(91)-O(7)-O(101)	109.4(10)
O(6)-O(7)-O(82)	112.8(24)	O(81)-O(7)-O(82)	134.7(13)
O(91)-O(7)-O(82)	37.4(20)	O(101)-O(7)-O(82)	72.7(21)
O(6)-O(7)-O(92)	104.5(17)	O(81)-O(7)-O(92)	24.3(20)
O(91)-O(7)-O(92)	90.9(20)	O(101)-O(7)-O(92)	133.8(20)
O(82)-O(7)-O(92)	122.3(27)	O(6)-O(7)-O(102)	103.8(14)
O(81)-O(7)-O(102)	87.1(17)	O(91)-O(7)-O(102)	135.6(15)
O(101)-O(7)-O(102)	29.2(16)	O(82)-O(7)-O(102)	101.0(25)
O(92)-O(7)-O(102)	111.2(25)	O(7)-O(81)-O(92)	81.8(47)
O(7)-O(91)-O(82)	58.3(33)	O(7)-O(101)-O(82)	48.6(18)
O(7)-O(101)-O(102)	83.4(28)	O(82)-O(101)-O(102)	130.0(33)
O(7)-O(82)-O(91)	84.3(36)	O(7)-O(82)-O(101)	58.7(20)
O(91)-O(82)-O(101)	141.4(51)	O(7)-O(92)-O(81)	73.8(41)
O(7)-O(102)-O(101)	67.5(38)	O(5)-O(11)-O(6)	121.0(7)
O(5)-O(11)-O(12)	118.5(6)	O(6)-O(11)-O(12)	120.5(6)
O(11)-O(12)-O(13)	106.3(7)	O(11)-O(12)-O(14)	111.3(7)
O(13)-O(12)-O(14)	112.4(7)	O(11)-O(12)-O(15)	110.0(7)
O(13)-O(12)-O(15)	108.1(8)	O(14)-O(12)-O(15)	108.7(7)
O(13)-O(16)-O(17a)	121.4(12)	O(18)-O(17)-O(16a)	120.1(12)
O(15)-O(18)-O(17)	118.4(12)		

Figure 3.5: The structure of  $\text{TiCl}_4(\text{CH}_3)_2\text{CCO}_2\text{H}$



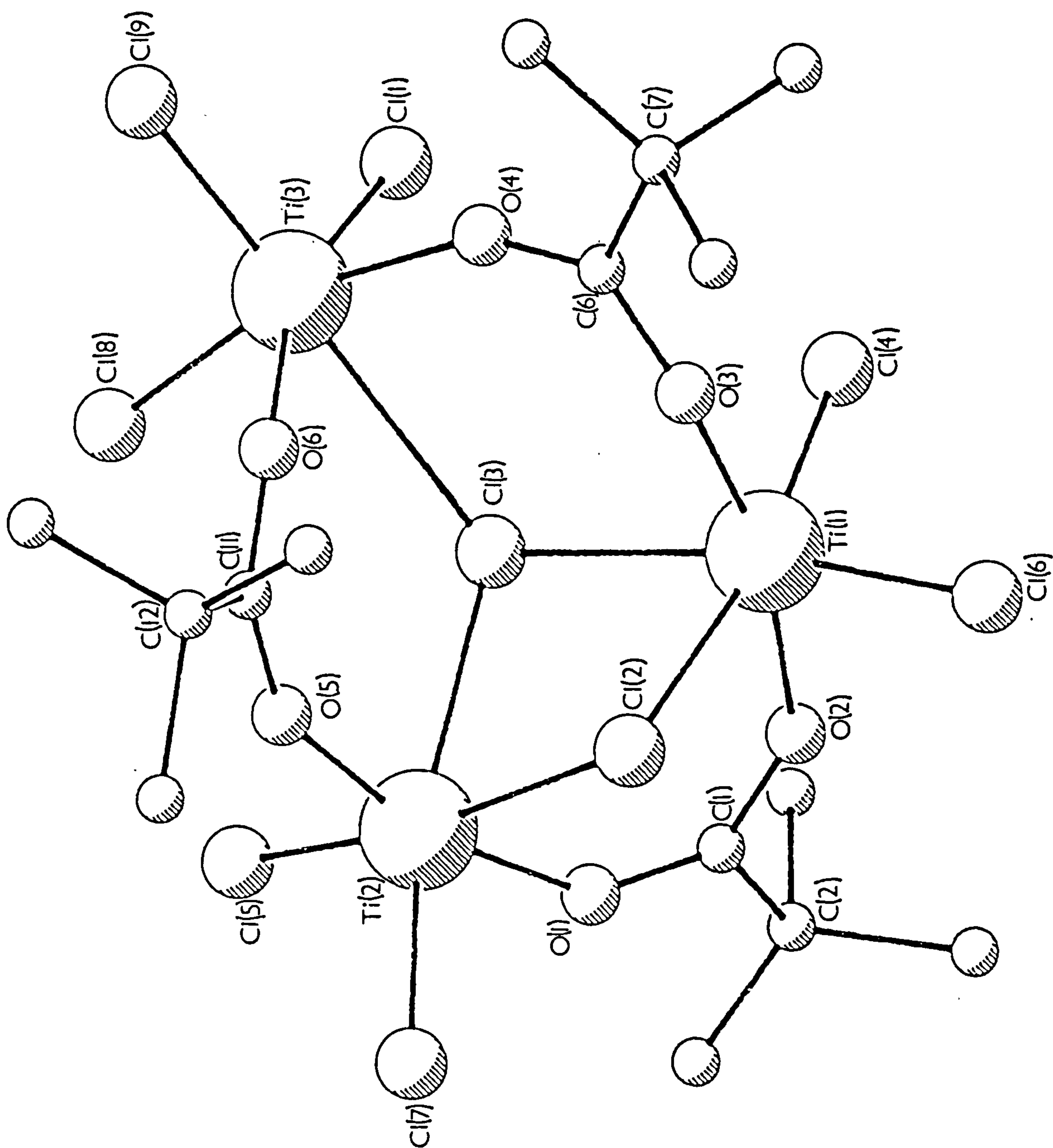


Figure 3.5: The structure of  $\text{Ti}_3\text{Cl}_9[(\text{CH}_3)_3\text{CCO}_2]_3$

The Ti-Cl bridge region has elongated (Ti-Cl-Ti angles are more than  $90^\circ$ ) and the angle between the terminal chlorines has opened up. The Ti(1) - Cl(3) - Ti(2) angle of  $94.7^\circ$  (cf. the Ti(1) - Cl(2) - Ti(2) angle of  $99.2^\circ$ ) shows distortion of the bridge as Cl(3) is bonded to Ti(3) as well as Ti(1) and Ti(2). The angles between the terminal chlorines attached to the titanium atoms have opened from the ideal  $90^\circ$  as shown in Table 3.5

**Table 3.5:**                      **Angles between terminal chlorines.**

Atoms	Angle
Cl(4) - Ti(1) - Cl(6)	$100.6^\circ$
Cl(5) - Ti(2) - Cl(7)	$101.3^\circ$
Cl(1) - Ti(3) - Cl(9)	$99^\circ$
Cl(8) - Ti(3) - Cl(9)	$101.3^\circ$
Cl(1) - Ti(3) - Cl(8)	$97.3^\circ$

This angle opening is as described by Hoffmann<sup>(140)</sup> who suggested sp rehybridisation opens up the angle between the terminal ligands after closed shell repulsions have stretched the bridging region.

The Cl(2) - Cl(3) distance of  $3.209\text{\AA}$  is longer than the bridging chlorine separation found in  $(\text{TiCl}_4\cdot\text{EtOAc})_2$  ( $3.18\text{\AA}$ )<sup>(82)</sup> or  $\text{Ti}_2\text{Cl}_{10}^{2-}$  ( $3.165\text{\AA}$ )<sup>(142)</sup> again showing distortion of the bridge due to the influence of Ti(3).

The carboxylate bridging Ti(1) and Ti(2) is reasonably symmetrical with Ti-O bond lengths of  $1.953$  and  $1.965\text{\AA}$  and C-O bond lengths of  $\sim 1.26\text{\AA}$ . The other two carboxylate ligands are unsymmetrical. The Ti-O bond lengths of Ti(3) are longer than those of Ti(1) or Ti(2). The Ti(3) -O bond

lengths are  $\sim 1.98\text{\AA}$  and the Ti -O bond lengths for the other titaniums are  $\sim 1.88\text{\AA}$ . The C-O bond lengths are also unequal, one C-O bond being longer than the other within the same carboxylate group.

All of the carboxylate ligands have O-C-O bond angles of  $121\text{--}123^\circ$ . These values are as expected from comparison with previous carboxylate structures<sup>(33)</sup>.

## DISCUSSION

The trimeric nature of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  in the solid state may be used to explain much of the spectral data previously reported for this compound.

### Infra-red spectra

The presence of two sets of carboxylate stretching frequencies in the infra-red spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  may be explained as there are two slightly different types of bridging carboxylates in the compound. The crystal structure of the compound revealed that a single molecule of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  contains a carboxylate symmetrically bridging two titaniums linked by two chlorine bridges and two asymmetric carboxylate bridges linking the  $\text{Ti}_2$  unit to the third titanium of the trimer.

The symmetric carboxylate bridge has both Ti-O bond lengths equal and both C-O bond lengths equal, whereas in the asymmetric carboxylate bridge these bond lengths differ. The two sorts of bridge will have different  $\text{CO}_2$ -stretching frequencies in the infra-red due primarily to the unequal C-O bond lengths of the asymmetric carboxylate. Therefore two  $\Delta$  values will be obtained from the infra-red spectrum. These values will be similar as

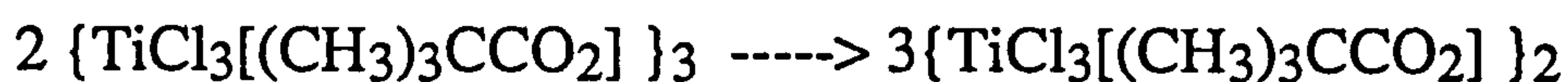


both carboxylates are still bidentate bridging. The  $\Delta$  values found in the infra-red spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  are  $125\text{cm}^{-1}$  and  $135\text{cm}^{-1}$ . These  $\Delta$  values are reasonable for the presence of two slightly different bidentate bridging carboxylates.

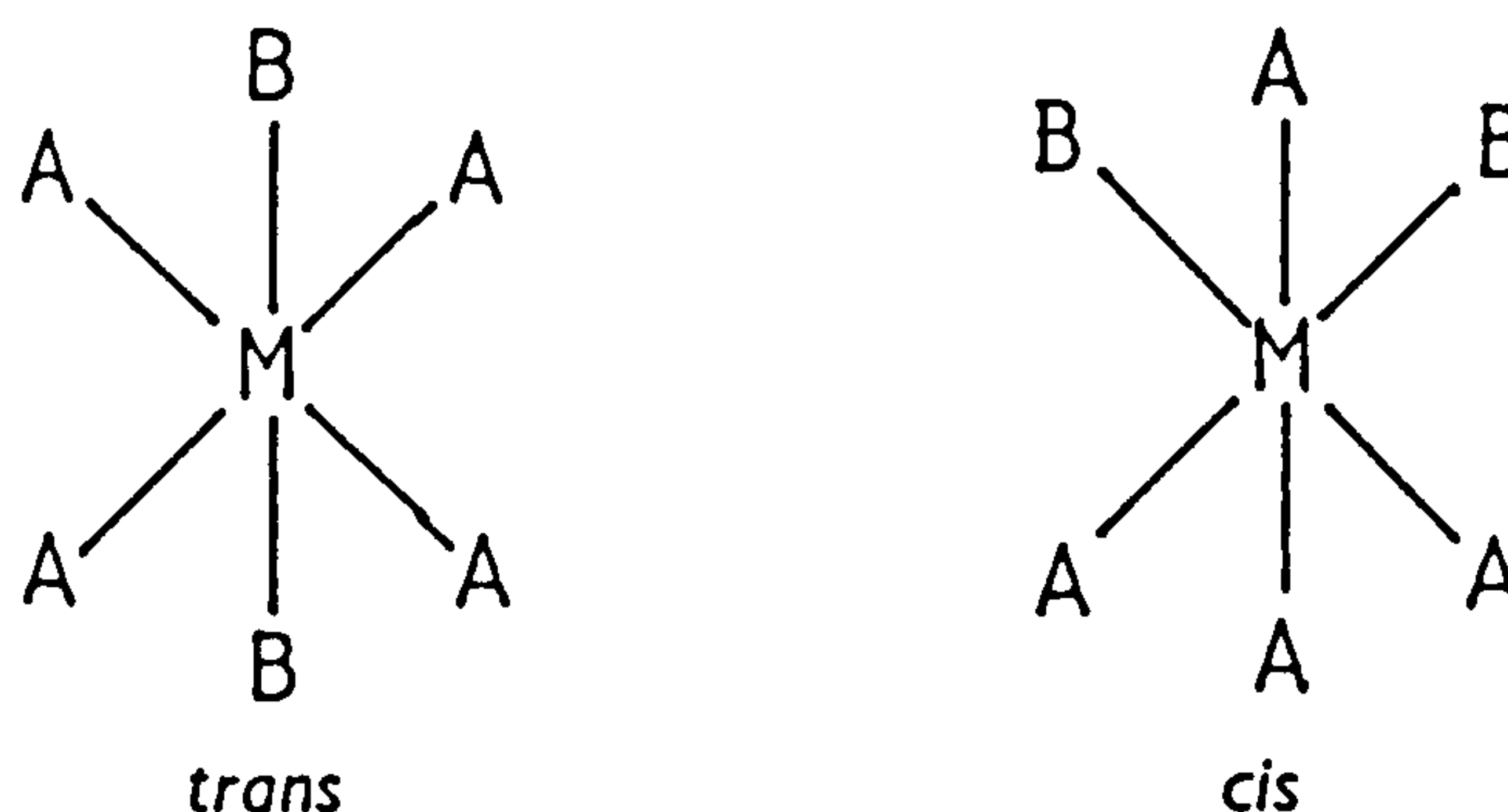
### $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

The proton NMR spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  contains multiple peaks around 1.1 - 1.55 p.p.m. Decoupling experiments have shown that these peaks do not arise from proton spin-spin coupling. Therefore each resonance must be due to a different species.

The compound is trimeric in the solid state but cryoscopic measurements indicate that it is dimeric in solution.. The trimer must dissociate into dimers upon dissolution. Simplistically this may occur as in the equation below:



However in the trimer two of the titanium centres are trans  $\text{MA}_4\text{B}_2$  systems and the third is a cis  $\text{MA}_4\text{B}_2$  system, as shown in Figure 3.6.



**Figure 3.6:**  $\text{MA}_4\text{B}_2$  Systems

Upon dissolution the two *trans* titanium atoms will form a dimer as they are already joined by chlorine and carboxylate bridges. The third titanium cannot dimerise as its *cis* configuration is not correctly orientated to form chlorine bridges. This titanium must isomerise from *cis* to *trans* before a dimer can form. Isomerisation may occur through formation of four or five coordinate chelated species as shown in Figure 3.7.

As the formation of chelating carboxylates is unfavourable the isomerisation will be slow and a number of different species and transition states, which give different resonances in the  $^1\text{H}$  NMR spectrum, will be formed.

The titanium crotonate derivative,  $\text{Ti}_2\text{Cl}_7(\text{CH}_3\text{CH}=\text{CHCO}_2)(\text{CH}_3\text{CH}=\text{CHCOOH})$  may model one of the species present in solution. The complex represents a dimeric residue where attack by  $\text{HCl}$  has occurred before the pendent oxygen atom of the carboxylate residue can bond to titanium forming the di- $\mu$ -carboxylato species.

Heating will increase the rate of interconversion between the different species until interconversion is fast in comparison with the NMR time scale and only one resonance is observed. The variable temperature  $^1\text{H}$  NMR spectra of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  show merging of the resonances as the temperature is increased. At  $100^\circ\text{C}$  the resonances are in an intermediate - exchange pattern and it is expected that at higher temperatures only one resonance will be seen.

Another possible cause of the multiple peaks is carboxylate scrambling or exchange. This will increase in rate as the temperature is raised eventually giving single resonances. The contribution of scrambling and exchange

processes to the multiple resonances is probably small as multiple peaks have not been reported in the  $^1\text{H}$  NMR spectra of other metal pivalates. Carboxylate scrambling and exchange is shown in Figure 3.8.

The  $^{13}\text{C}$  NMR spectrum of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  does not show multiple peaks as the isomerisation and scrambling processes are fast compared to the  $^{13}\text{C}$  NMR time scale. This means that only single resonances will be observed.

### Mass Spectrum

The  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  trimer fragments within the probe and only  $\text{TiCl}_n$  ions and a single titanium carboxylate residue are distinguishable. No molecular ion could be identified.

### Molecular Structure

In the solid state  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  exists as a trimeric unit. This structure is unexpected since most  $\text{TiCl}_3\text{L}$  or  $\text{TiCl}_4\cdot\text{L}$  species are chlorine bridged dimers<sup>(143,87)</sup>. The predicted structure for  $\text{TiCl}_3(\text{RCO}_2)$  compounds is shown in Figure 3.9.



**Figure 3.7: Isomerisation and Dimerisation of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$**

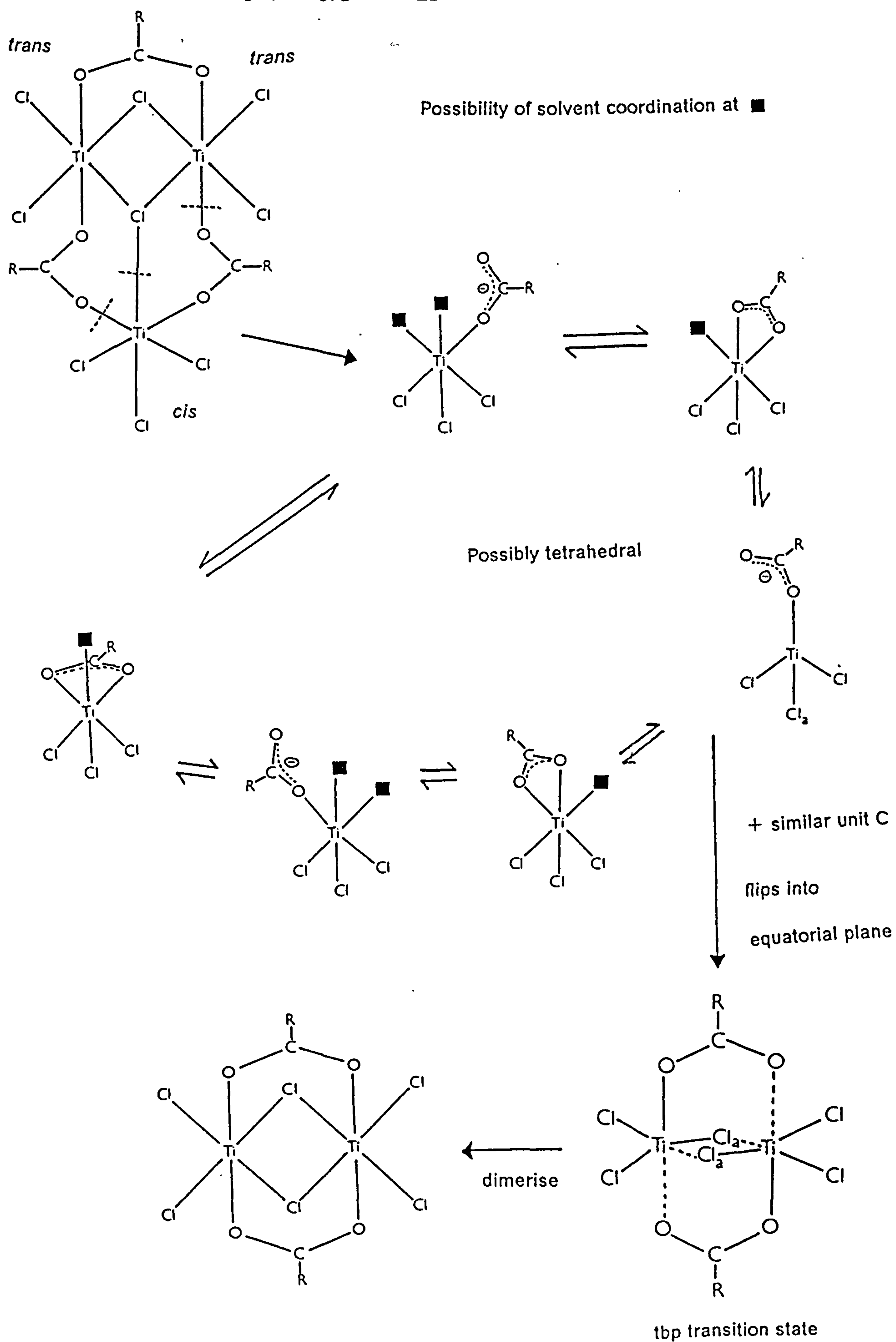
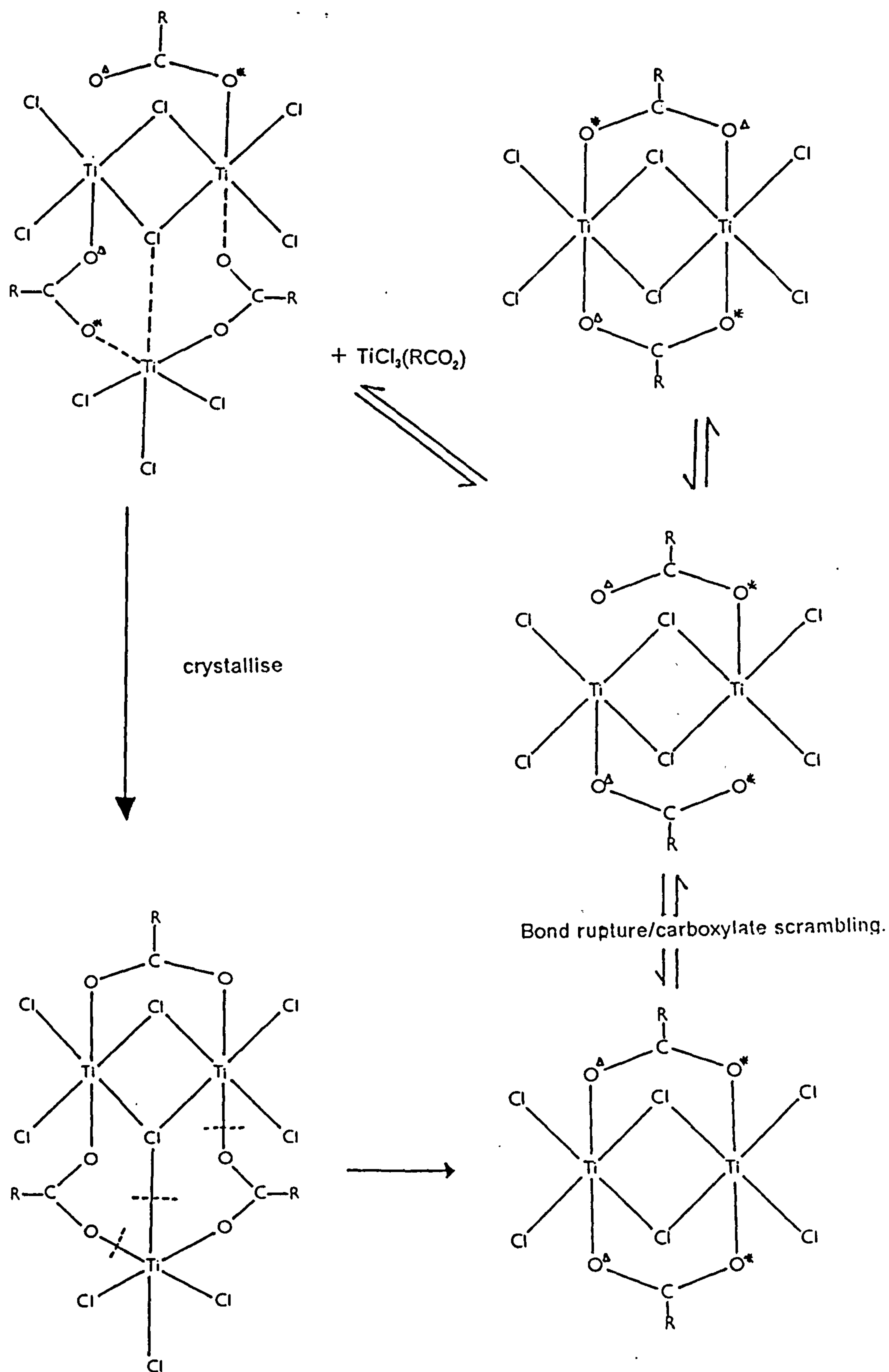
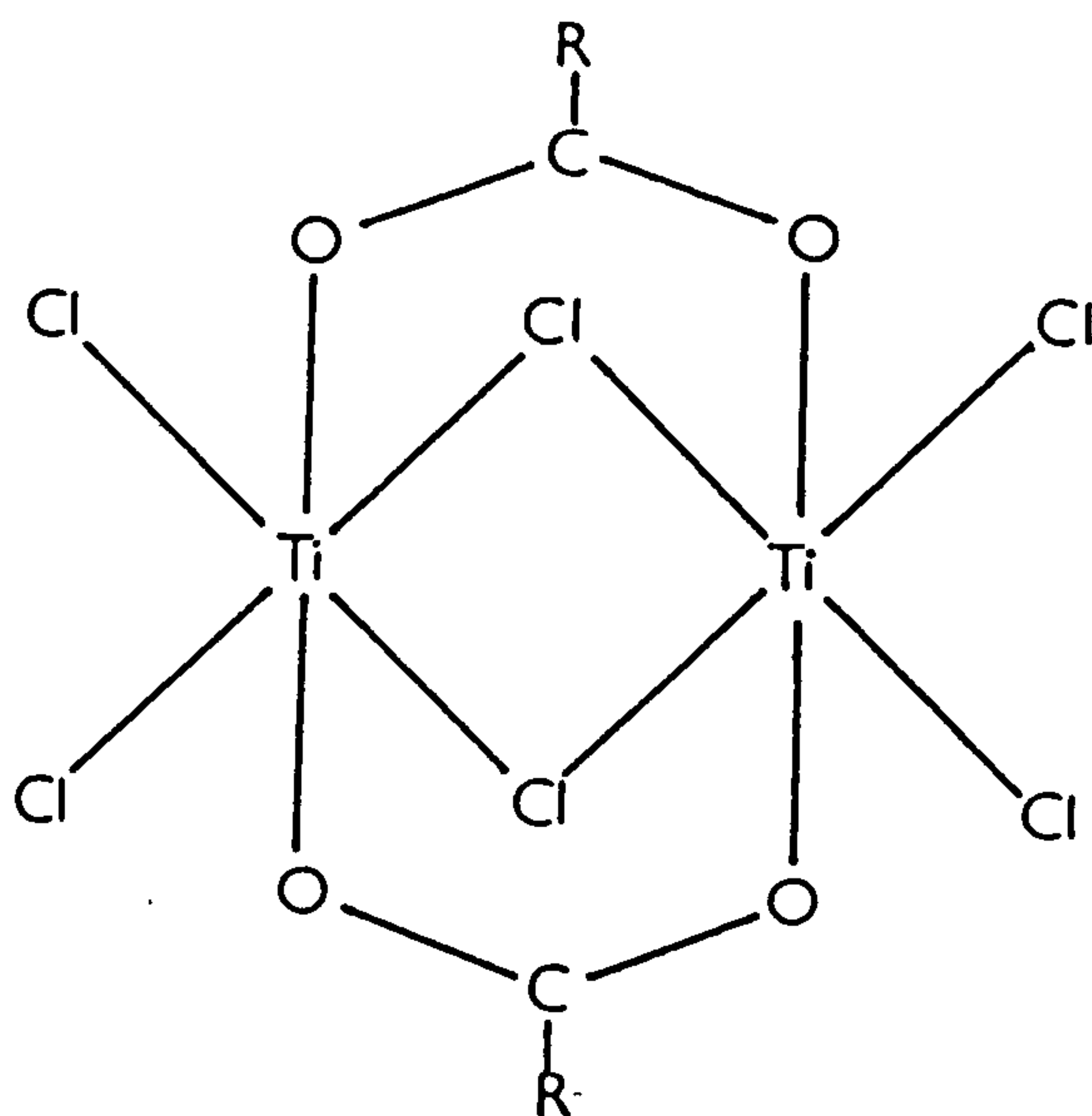




Figure 3.8: Carboxylate Scrambling and Exchange





**Figure 3.9 Dimeric Structure for  $\text{TiCl}_3 [(\text{CH}_3)_3\text{CCO}_2]$**

A possible explanation for the trimeric structure is provided by consideration of the coordination of each titanium atom.  $\text{Ti}(1)$  and  $\text{Ti}(2)$  are octahedrally coordinated with all the ligands in mutually *trans* positions,  $\text{Ti}(3)$  however achieves octahedral geometry by interaction with one of the chlorine atoms bridging  $\text{Ti}(1)$  and  $\text{Ti}(2)$  and is the *cis* stereoisomer.

It is known that the octahedral geometry is preferred for titanium (IV) complexes. It is therefore suggested that  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  forms a trimer in the solid to allow interaction between a bridging chlorine atom and the third titanium to complete the octahedral coordination of  $\text{Ti}(3)$ .

The presence of carboxylate ligands capable of bridging large interatomic distances allows the third titanium to be held in position for interaction with the bridging chlorine atom. It may be more energetically favourable to

have three six coordinate titanium atoms rather than two six coordinate and one five coordinate titanium atoms.

This structure may be compared to that of  $\text{SeOCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ <sup>(144)</sup> The selenium atom has square pyramidal coordination but a weak interaction between one chlorine atom and the selenium atom in a neighbouring molecule completes an octahedron. So there is secondary dimerisation in the solid state. The Se-Cl bond to the interacting chlorine is increased in length relative to the Se-Cl bond of the normal chlorine atom. A similar effect is observed in the structure of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$ , the Ti-Cl bond to the triply bridging chlorine atom being longer than that to the other bridging chlorine atom.

The carboxylate ligands bridging the  $\text{Ti}_2$  unit to the third titanium atom show signs of strain due to the long distance ( $4.5\text{\AA}$ ) being bridged. The Ti-O bonds to the third titanium are longer than those to the other two titanium atoms. This strain is probably the cause of the molecular dissociation in solution whereby the third titanium breaks away and achieves octahedral coordination using weakly bound solvent molecules.

The  $\text{Ti}_2\text{Cl}_6$  dichlorine bridged element of the trimer is similar to that found in many titanium (IV) complexes such as  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$ <sup>(139)</sup> In some other complexes the chlorine bridge is asymmetric, the chlorine atom being closer to one titanium centre than the other. In  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  the bridges are symmetric, the chlorine atoms being equidistant from the two titanium atoms. The chlorine bridges in  $(\text{TiCl}_4 \cdot \text{EtOAc})_2$  also have equal Ti-Cl bond lengths<sup>(82)</sup>

It is possible that other  $\text{TiCl}_3 \cdot \text{L}$  complexes where L is a ligand capable of bidentate bridging may have similar trimeric structures to that of

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  . The bridging ligands stabilised the trimers formed by titanium-chlorine interactions.

## Conclusions

A single crystal x-ray diffraction determination has shown that  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  is trimeric in the solid state with the three titanium atoms joined by carboxylate and chlorine bridges. In solution the compound dissociates into dimers. Its behavior in solution is very complex with many different species being formed and interconverting.



**CHAPTER 4**

**HYDROLYSIS REACTIONS**

**OF**

**TiCl<sub>3</sub>(RCO<sub>2</sub>) COMPLEXES**

## INTRODUCTION

Titanium (IV) halides and complexes are easily hydrolysed. Little is known about the intermediates involved in their hydrolysis. We have investigated the hydrolysis of titanium (IV) monocarboxylates in a coordinating solvent such as ethyl acetate or tetrahydrofuran. This is an extension of the work previously reported by Gordon<sup>(128)</sup> who prepared  $[\text{TiCl}_2(\text{RCO}_2)\text{L}]_2\text{O}$  ( $\text{R} = \text{C}_6\text{H}_5, \text{CH}_3$ ;  $\text{L} = \text{THF}$  or  $\text{EtOAc}$ ).

### Titanium Oxo-Compounds

Titanium forms strong metal-oxygen bonds, often by hydrolysis of Ti(IV) compounds. A considerable number of complexes containing Ti-O groups have been reported. Most of these complexes are polynuclear species with bridging oxygens.

Some non-bridging  $\text{Ti}=\text{O}$  units have been reported. The titanium porphyrin complex  $\text{TiO}(\text{OEPMe}_2)$  contains a distinct  $\text{Ti}=\text{O}$  moiety with a short Ti-O bond length.<sup>(145)</sup> A similar  $\text{Ti}=\text{O}$  unit is found in the porphyrin complex  $\text{TiO}(\text{OEP})$ .<sup>(146)</sup> The complexes  $\text{TiCl}_4\text{O}(\text{Et}_4\text{N})_2$ ,  $\text{TiCl}_4\text{O}(\text{Me}_4\text{N})_2$  and  $\text{TiCl}_4\text{O}(\text{NH}_3\text{C}_2\text{H}_5)_2$  were made by Feltz.<sup>(147)</sup> The  $\text{Ti}=\text{O}$  bond in the infra-red spectrum of the  $\text{TiCl}_4\text{O}(\text{NH}_3\text{C}_2\text{H}_5)_2$  complex had a  $\text{Ti}=\text{O}$  band at  $830\text{cm}^{-1}$ . The X-ray crystal structure of the  $\text{TiCl}_4\text{O}(\text{Et}_4\text{N})_2$  complex shows the titanium slightly above the plane of the four chlorine atoms and capped by the oxygen atom. The complex is a tetragonal pyramid.<sup>(148)</sup> The structure of  $\text{TiCl}_4\text{O}^{2-}$  is shown in Figure 4.1.

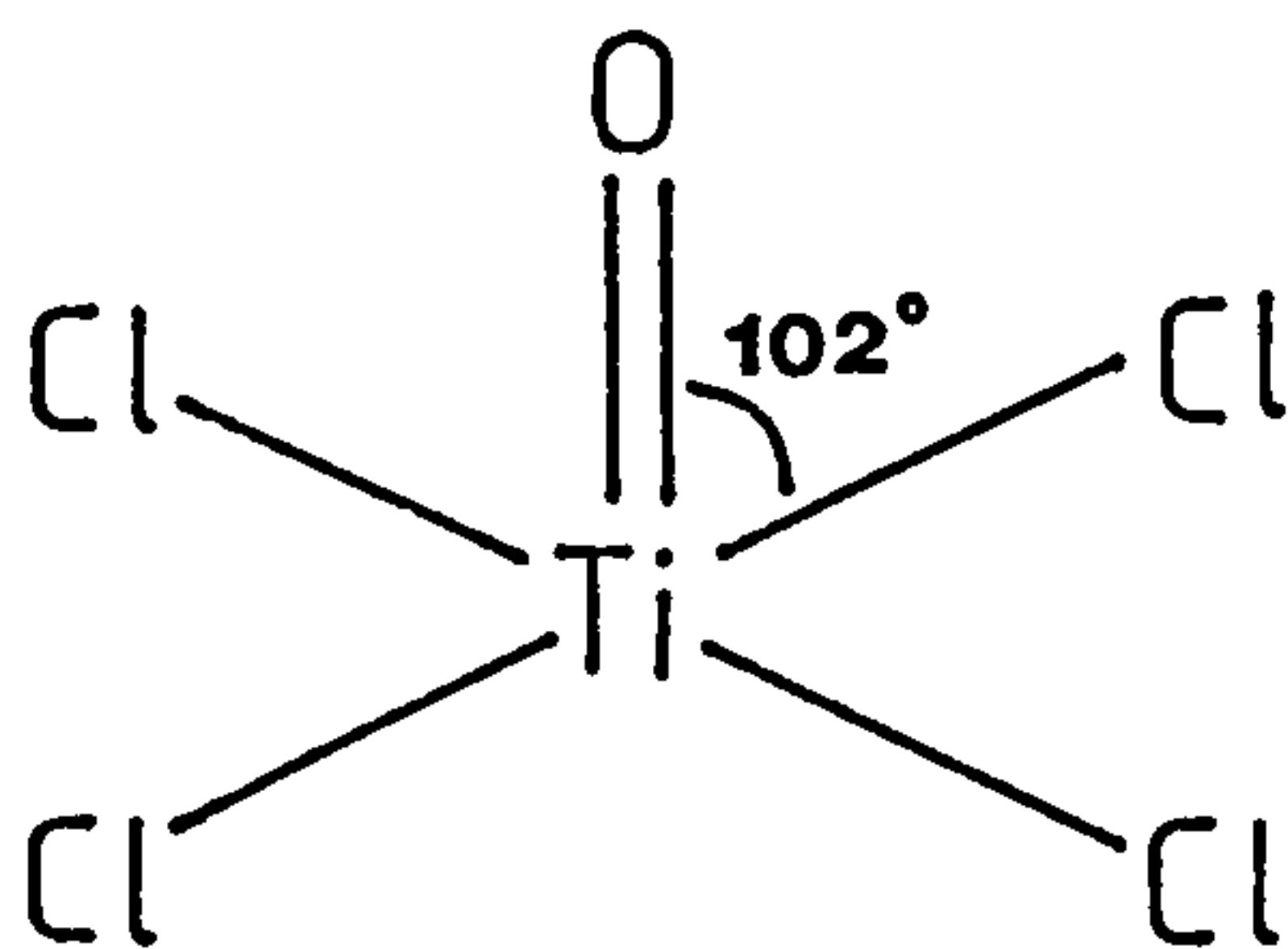


Figure 4.1 The Structure of the  $\text{TiCl}_4\text{O}_2^-$  Anion.

Most titanium oxo-compounds contain oxygen bridges forming oligomers. The partial hydrolysis of  $\text{TiCl}_2(\text{acac})_2$  produces a number of oxygen bridged complexes. The solvated complex  $[\text{TiCl}(\text{C}_5\text{H}_7\text{O}_2)_2]_2\text{O} \cdot \text{CHCl}_3$  has two  $\text{TiCl}(\text{C}_5\text{H}_7\text{O}_2)_2$  units joined by an oxygen bridge. It was suggested that the Ti-O bonds have partial double-bond character<sup>(88)</sup> The complexes  $[\text{TiO}(\text{acac})_2]_2$  and  $[\text{TiO}(\text{acac})_2]_2 \cdot 2\text{C}_4\text{H}_8\text{O}_2$  have two oxygen bridges joining the titanium atoms<sup>(149)</sup> The structure of  $[\text{TiO}(\text{acac})]_2$  is shown in Figure 4.2.

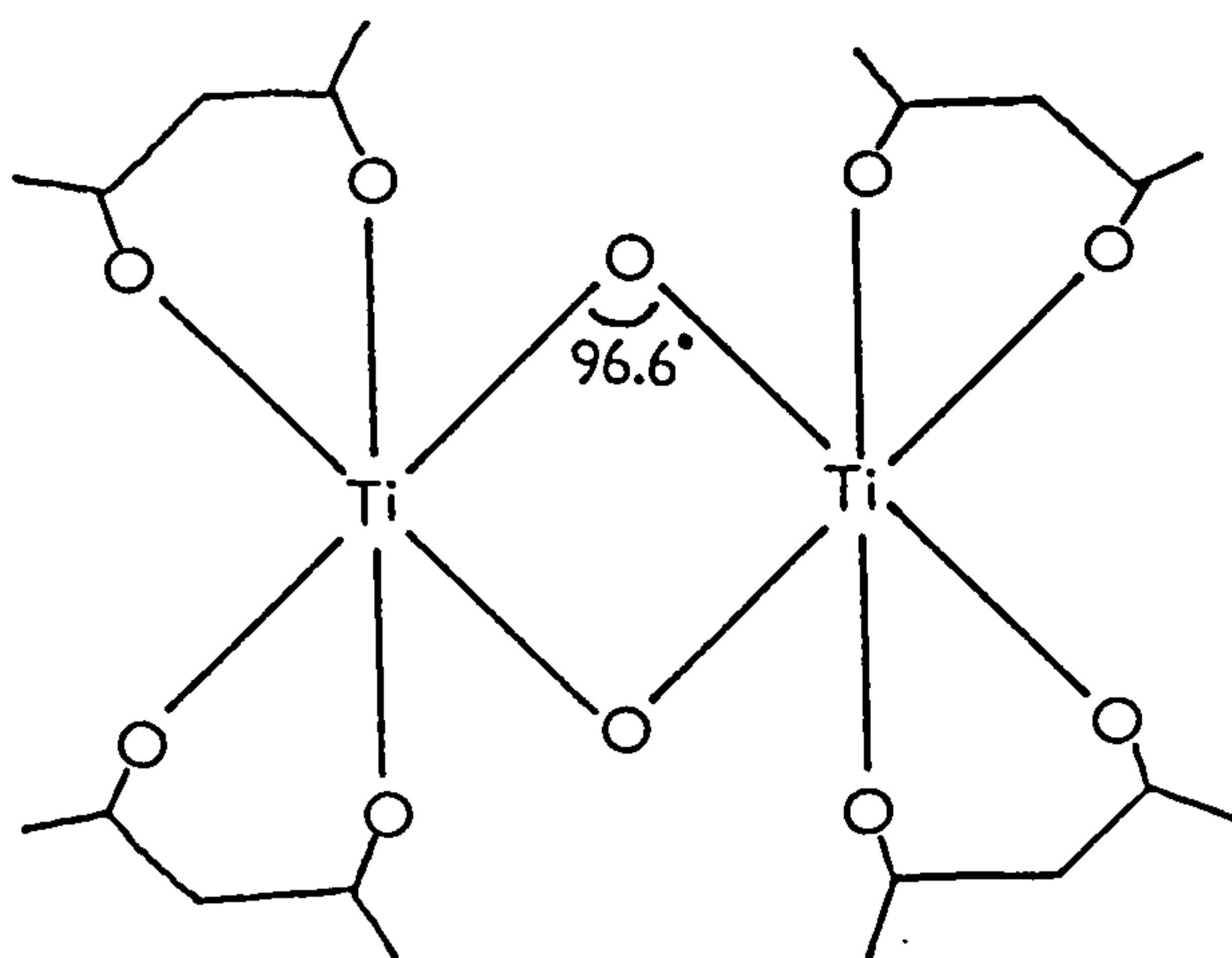


Figure 4.2: The Structure of  $[\text{TiO}(\text{acac})_2]_2$

Other oxygen bridged dimers which have been structurally characterised by X-ray methods include  $[(\text{Cp}_2\text{TiCl})_2\text{O}]$ <sup>(150)</sup> and  $[\text{Cp}_2\text{Ti}(\text{C}_9\text{H}_7\text{N})]_2\text{O}_2^+$ . The

Ti-O-Ti bridge in the cation is almost linear the bond angle being  $174.6^\circ$  (151) The complex  $[\text{Cp}_2\text{TiCl}]_2\text{O}$  was prepared by Giddings (152)

An unusual  $\text{M}_3\text{O}_3$  ring is found in the structure of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}(\mu\text{-O})_3]$ . The complex is made by hydrolysis of  $(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_3$  in benzene or hexane solution (153) The structure of the  $\text{Ti}_3\text{O}_3$  unit is shown in Figure 4.3.

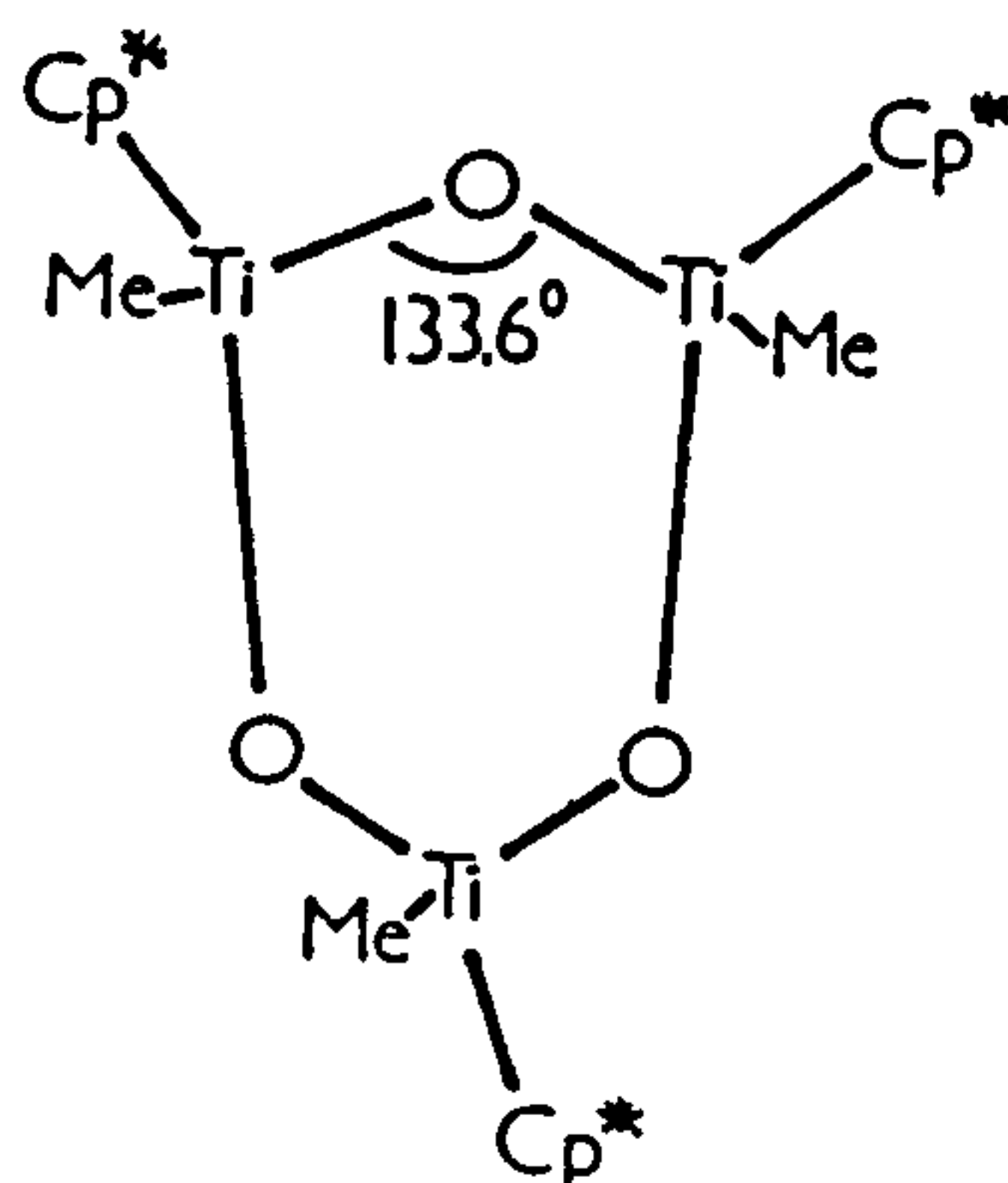


Figure 4.3: The Structure of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}(\mu\text{-O})_3]$

Some oxo-bridged compounds containing four titanium atoms have been structurally characterised. Ammonium titanyl oxalate  $[(\text{NH}_4)_2 \text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}]_4$  contains an eight membered ring of titanium and bridging oxygen atoms (154) The ring consists of two intersecting planes of titanium and oxygen atoms. This is shown in Figure 4.4.

A similar eight membered ring with alternating titanium and oxygen atoms is found in  $\text{Cs}_4[\text{Ti}_4\text{O}_4(\text{C}_6\text{H}_6\text{NO}_6)_4] \cdot 6\text{H}_2\text{O}$  (155)

Hydrolysis of  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{TiCl}_3$  produces  $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{TiCl}(\mu\text{-O})]_4$ . This compound contains an eight membered ring composed of four titanium atoms bridged by oxygens (156) Hydrolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3$  gives the similar compound  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}(\mu\text{-O})]_4$  (157) The generalised structure of these compounds is shown in Figure 4.5.



An unusual  $[\text{Ti}_4(\mu\text{-O})_6]^{4+}$  cation with an adamantane type structure is found in  $[\text{Ti}_4(\text{C}_6\text{H}_{15}\text{N}_3)_4(\mu\text{-O})_6]\text{Br}_4 \cdot 4\text{H}_2\text{O}$ . The  $\text{Ti}_4\text{O}_6$  unit has a strong infra-red band at  $730\text{cm}^{-1}$ .<sup>(158)</sup>

### $\text{M}_2(\mu\text{-O})(\mu\text{-RCO}_2)_2$ Cores

Partial hydrolysis of  $\text{TiCl}_3(\text{RCO}_2)$  or  $\text{TiCl}_2(\text{RCO}_2)_2$  species ( $\text{R} = \text{C}_6\text{H}_5, \text{CH}_3$ ) in a coordinating solvent such as tetrahydrofuran or ethyl acetate produces binuclear complexes,  $[\text{TiCl}_2(\text{RCO}_2)_2\text{L}]_2\text{O}$ , containing a  $\mu$ -oxo-di- $\mu$ -carboxylate core.<sup>(159)</sup> Similar  $[\text{M}_2(\mu\text{-O})(\mu\text{-RCO}_2)_2]^{n+}$  units are found in a number of other metal complexes.

The  $\mu$ -oxo-di- $\mu$ -carboxylato core is found in complexes of  $\text{Fe(III)}$ <sup>(160)</sup>,  $\text{Mn(III)}$ <sup>(161)</sup>,  $\text{V(III)}$ <sup>(162)</sup>,  $\text{Os(IV)}$ <sup>(163)</sup> and the mixed valence species  $\text{Mn(III)-Mn(IV)}$ .<sup>(164)</sup> Many of these complexes were synthesized as models for the metal centres in metalloproteins such as hemerythrin. The structure of  $[\text{TiCl}_2(\text{C}_6\text{H}_5\text{CO}_2)\text{EtOAc}]_2\text{O}$  is shown in Figure 4.6.

The  $\text{Os(IV)}$  derivative  $[\text{OsCl}_2(\text{CH}_3\text{CO}_2)\text{PPh}_3]_2\text{O}$ , is the closest parallel to the  $\text{Ti(IV)}$  complex. Most of the other compounds which contain the  $\mu$ -oxo-di- $\mu$ -carboxylato core are stabilised by macrocyclic ligands. In the titanium (IV) complex the ligands are *trans* to the bridging oxygen however in the osmium (IV) complex the phosphine ligands are *trans* to a carboxylate oxygen and a chlorine is *trans* to the bridging oxygen.<sup>(163)</sup> The structure of  $[\text{OsCl}_2(\text{CH}_3\text{CO}_2)\text{PPh}_3]_2\text{O}$  is shown in Figure 4.7.

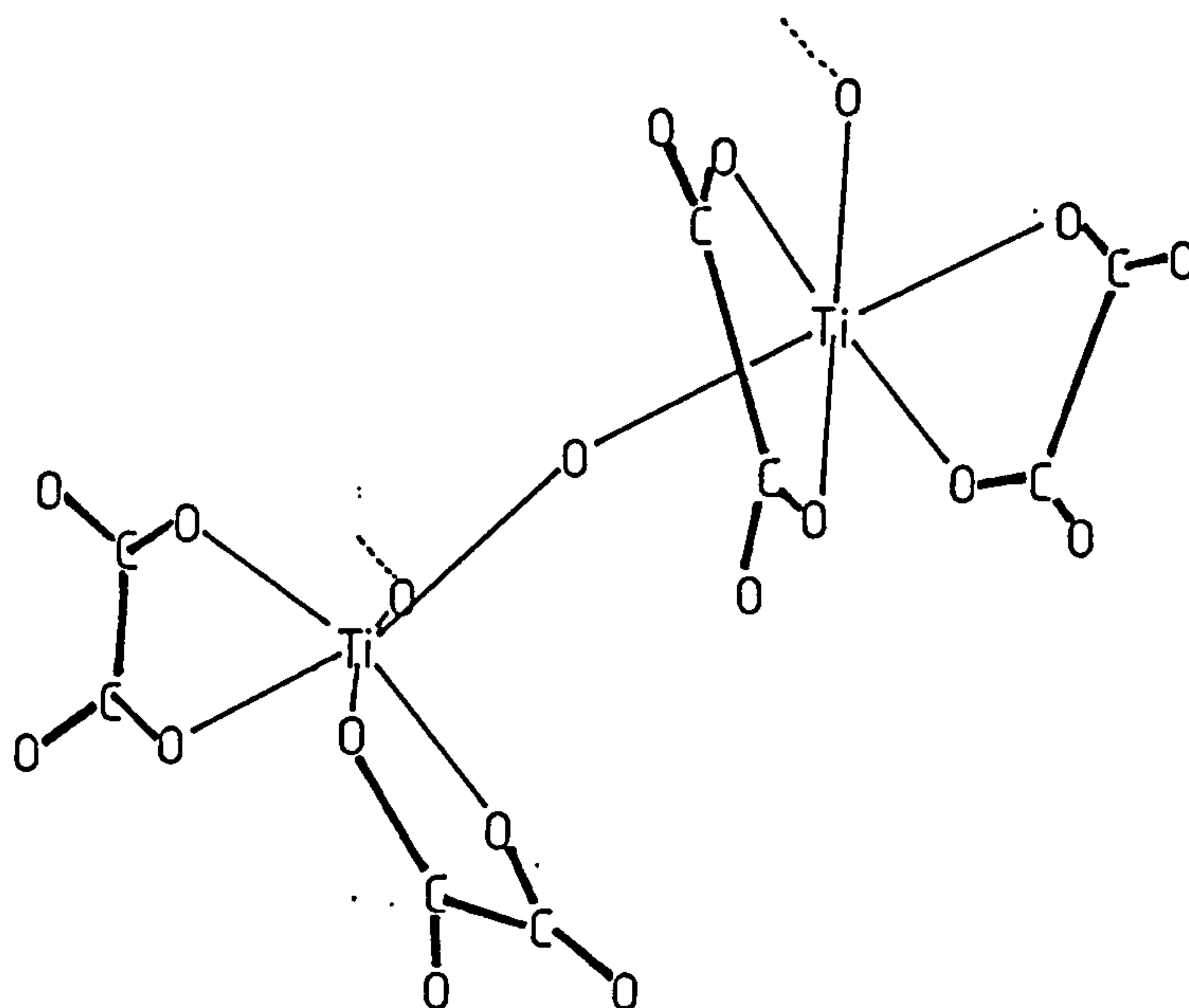


Figure 4.4. The Ti-O ring in  $[(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}]_4$

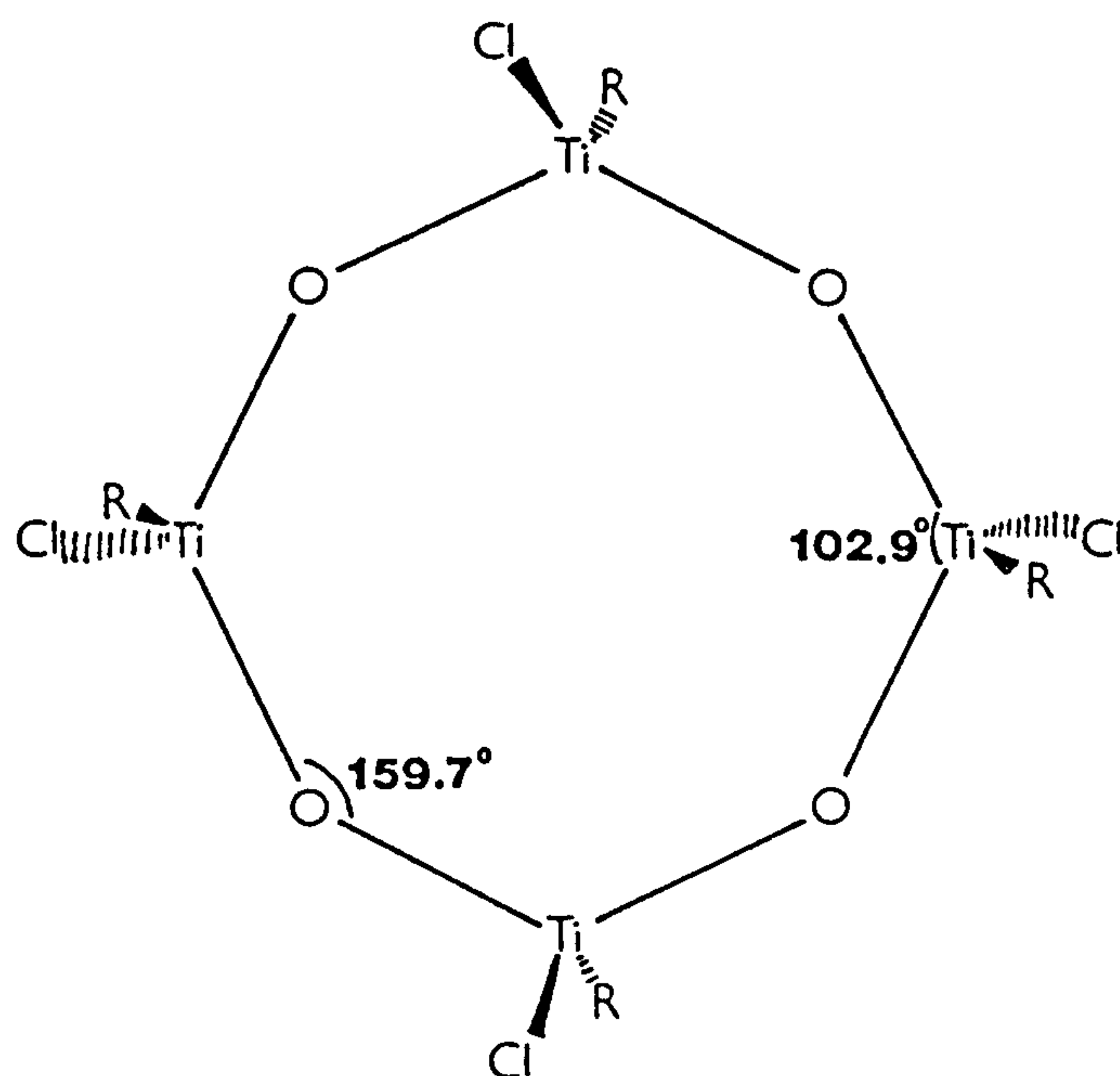
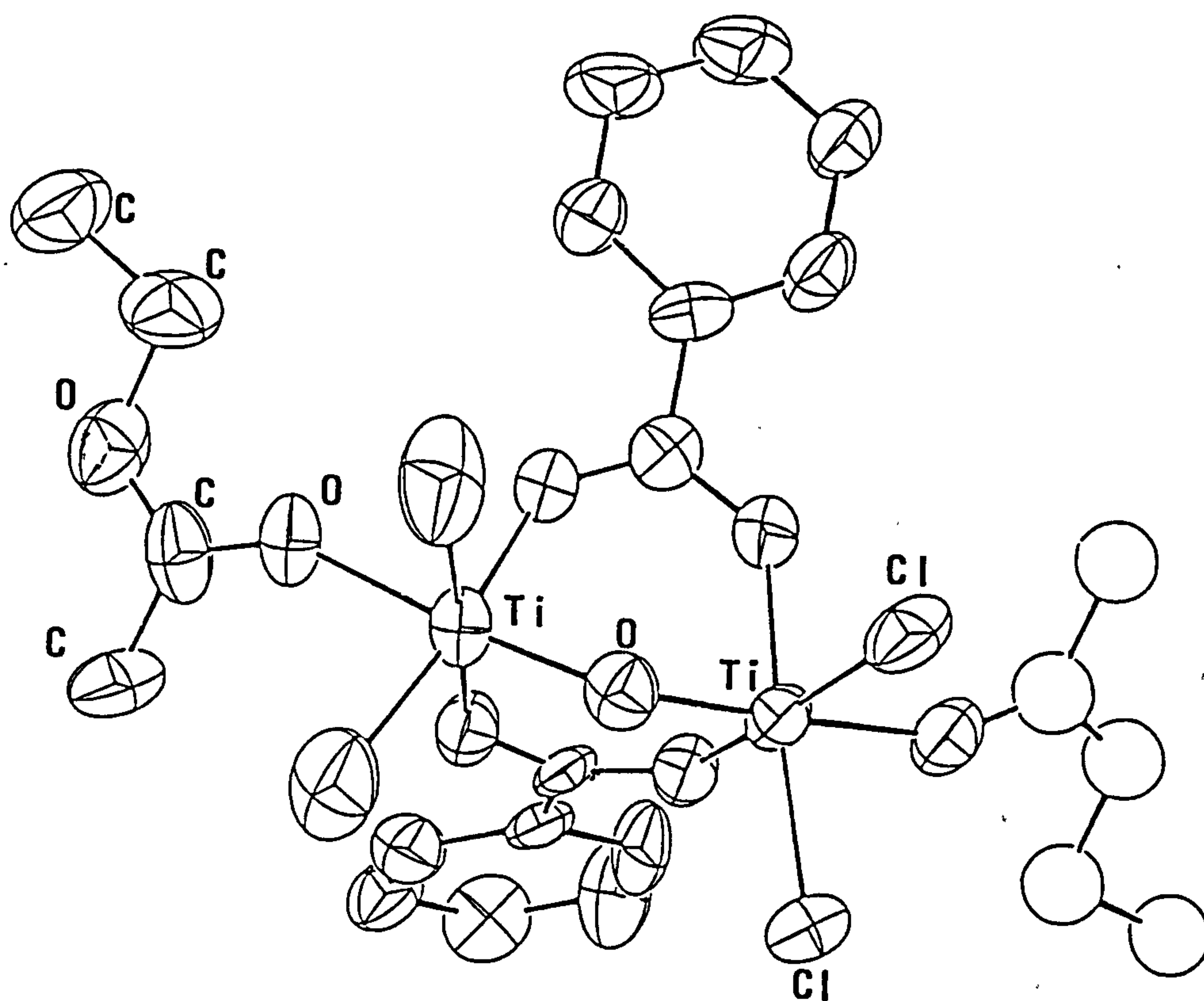


Figure 4.5. The structure of  $[(\eta^5\text{-R})\text{TiCl}(\mu\text{-O})]_4$  ( $\text{R}=\text{C}_5\text{H}_5$  or  $\text{CH}_3\text{C}_5\text{H}_4$ )

Figure 4.6 The structure of  $[\text{TiCl}_2(\text{C}_6\text{H}_5\text{CO}_2)\text{EtOAc}]_2\text{O}$



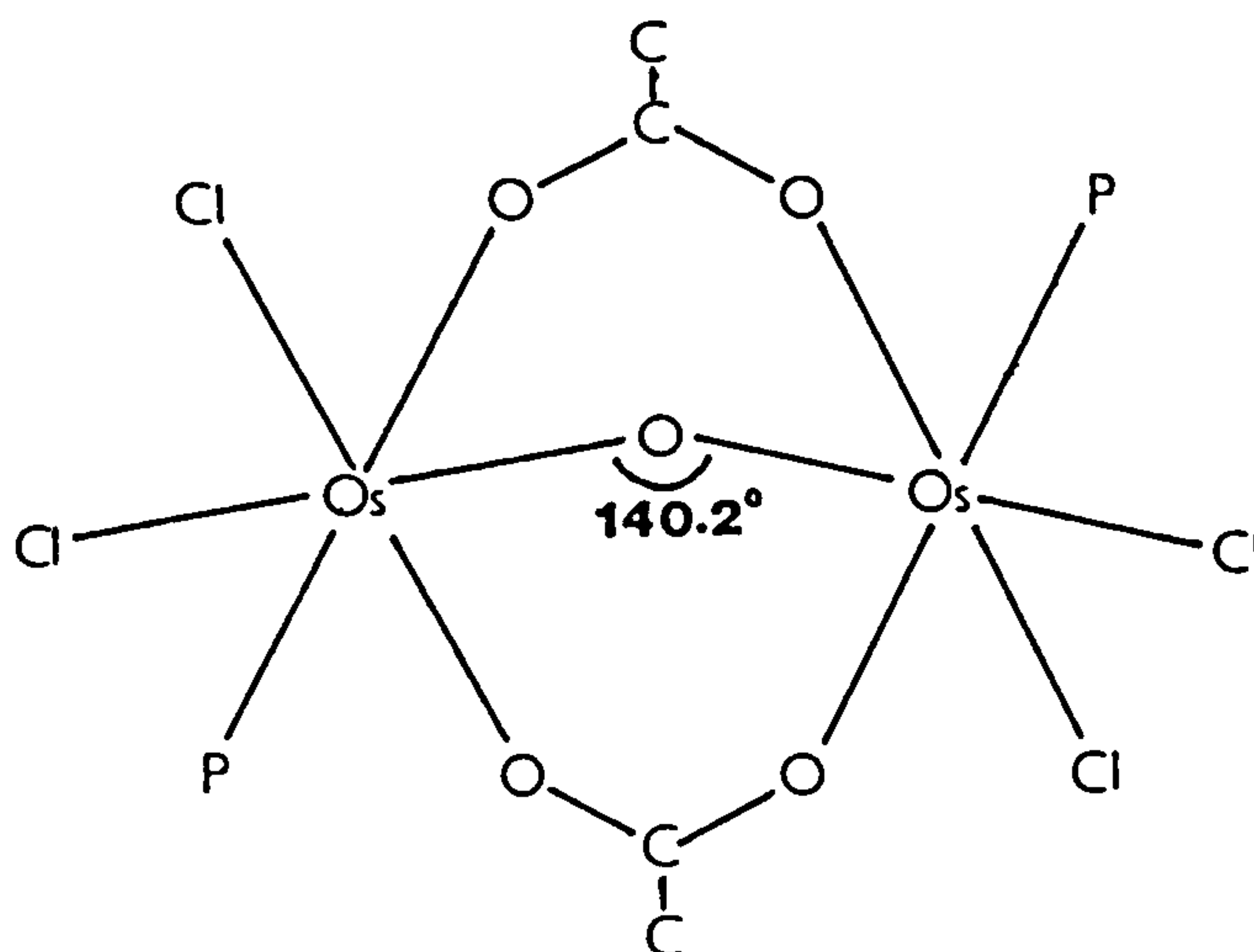


Figure 4.7. The Structure of  $[\text{OsCl}_2(\text{CH}_3\text{CO}_2)\text{PPh}_3]_2\text{O}$

The related  $\mu$ -hydroxo-di- $\mu$ -carboxylato core has been found in complexes of Fe(II)<sup>(165)</sup> and in the heterobimetallic complexes of Cr(III)-M(II), (M = Fe, Zn, Cu, Ni, Co, Mn). The bimetallic compounds were made using the  $[\text{LCr}(\text{solvent})_3]^{3+}$  cation as a reactant. L is 1,4,7-trimethyl - 1,4,7-triazacyclononane. X-ray crystal structures of the  $[\text{LCr}(\mu\text{-OH})(\mu\text{-CH}_3\text{CO}_2)_2\text{M}^{\text{II}}\text{L}]$  (M = Fe, Co) complexes were reported<sup>(166)</sup>

## PREPARATION OF TITANIUM OXO-COMPOUNDS

The partially hydrolysed complexes were prepared in this work by dissolution of the monocarboxylate in EtOAc or THF which contained the stoichiometric amount of water required. The resulting solution was stirred and the volume of solvent reduced until solid precipitated. The  $2\text{H}_2\text{O} : 1 \text{ Ti}$  hydrolysis product was recrystallised from dichloromethane. Using these conditions under careful control the yields of the oxocompounds were 70-80%.



An alternative was to dissolve the monocarboxylate in pyridine containing the required amount of water. This produced a hydrolysed titanium (IV) pyridine adduct.

The reaction of the monopivalate pyridine adduct with water in the ratio 2 Ti : 1 H<sub>2</sub>O gave a yellow solid and an orange solution. The yellow solid was unreacted starting material. An orange solid obtained from the orange solution was soluble in chlorinated solvents. Its <sup>1</sup>H NMR spectrum indicated the presence of 2 (CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub><sup>-</sup> residues to each pyridine.

The <sup>1</sup>H NMR spectrum of the 2H<sub>2</sub>O : 1 Ti hydrolysis product contains only resonances due to coordinated ethyl acetate. The carboxylate group has been displaced. Elemental analysis of the white solid indicates a formulation as Ti<sub>2</sub>Cl<sub>3</sub>(EtOAc)<sub>6</sub>O<sub>4</sub>.

The white solid obtained from the 1H<sub>2</sub>O:1Ti hydrolysis of TiCl<sub>3</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>] is very soluble in chlorinated solvents. Its <sup>1</sup>H NMR spectrum indicates the presence of equal amounts of (CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub><sup>-</sup> and EtOAc in the compound. The carbon and hydrogen analyses of the solid are close to those for {TiCl<sub>2</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>]EtOAc}<sub>2</sub>O. The Ti-O stretching region of the infra-red spectrum of the solid is very similar to that of the 2Ti : 1H<sub>2</sub>O hydrolysis product. Therefore it appears that the white solid is a mixture of {TiCl<sub>2</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>]EtOAc}<sub>2</sub>O and impurities.

Wiegardt and coworkers found that hydrolysis of [L<sub>2</sub>Mn<sub>2</sub>(μ-O)μ-MeCO<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> formed the di-μ-oxo-μ-acetato species [L<sub>2</sub>Mn<sup>III</sup>Mn<sup>IV</sup>(μ-O)<sub>2</sub>(μ-MeCO<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> (167) By analogy it was expected that the 1H<sub>2</sub>O : 1 Ti hydrolysis of titanium (IV) monocarboxylates would produce the anion [Ti<sub>2</sub>L<sub>2</sub>(μ-O)<sub>2</sub>(μ-RCO<sub>2</sub>)]<sup>-</sup>. This anion is not formed. It is possible that

addition of a counter-ion would allow formation of the di- $\mu$ -oxo- $\mu$ -carboxylato anion.

A number of complexes of the type  $[\text{TiCl}_2(\text{RCO}_2)\text{L}]_2\text{O}$  were prepared. The carboxylates used were the benzoate, pivalate and *p*-toluate. The benzoate derivative had previously been made by Gordon<sup>(128)</sup>

### **$^{17}\text{O}$ NMR Studies of $[\text{TiCl}_2(\text{RCO}_2)\text{EtOAc}]_2\text{O}$**

The oxo bridge in  $[\text{TiCl}_2(\text{RCO}_2)\text{EtOAc}]_2\text{O}$  complexes may be enriched with  $^{17}\text{O}$  by performing the hydrolysis of the monocarboxylate with  $\text{H}_2\text{O}^{17}$ . When  $\text{TiCl}_3(\text{PhCO}_2)$  is hydrolysed with  $\text{H}_2\text{O}^{17}$  the  $^{17}\text{O}$  NMR spectrum of the crystalline product contains a sharp singlet at +810 p.p.m. (relative to  $\text{H}_2\text{O} = 0$ ) due to the  $\mu$ -oxo bridge<sup>(159)</sup>

The solution behavior of  $[\text{TiCl}_2(\text{RCO}_2)\text{EtOAc}]_2\text{O}$  ( $\text{R} = \text{Ph}, (\text{CH}_3)_3\text{C}$ ) in EtOAc was investigated by  $^{17}\text{O}$  NMR spectroscopy. The carboxylate was dissolved in EtOAc which contained the appropriate amount of  $\text{H}_2\text{O}^{17}$  for  $2\text{Ti} : 1\text{H}_2\text{O}$ . The  $^{17}\text{O}$  NMR spectra of the solutions were then measured.

Resonances due to the bulk ethyl acetate were observed at  $\sim 363$  p.p.m. and 171 p.p.m. The resonance at 363 p.p.m. was due to the carbonyl oxygen and the resonance at 171 p.p.m. due to the ether type oxygen. Multiple resonances were observed in the region 800-900 p.p.m., these are reported in table 4.1. By comparison with the  $^{17}\text{O}$  NMR spectra reported for vanadium (V) complexes containing bidentate oxygen bridges<sup>(168)</sup> the multiple resonances are assigned to oxygens bridging two titanium atoms.



The  $^{17}\text{O}$  NMR spectrum of the solid extracted from the solution containing  $\{\text{TiCl}_2(\text{RCO}_2)\text{EtOAc}\}_2\text{O}$  has a sharp singlet at 853 p.p.m. The resonance at 853 p.p.m. is therefore assigned to the bridging oxygen of  $\{\text{TiCl}_2(\text{RCO}_2)\text{EtOAc}\}_2\text{O}$ .

It has been suggested that the  $^{17}\text{O}$  chemical shifts of bidentate oxygen bridges have an inverse dependence upon the angle  $\text{M-O-M}$ .<sup>(169)</sup> It is proposed that the other resonances found between 800-900 p.p.m. in the  $^{17}\text{O}$  NMR spectra of the  $\mu$ -oxo-di- $\mu$ -carboxylato species are due to related complexes with slightly different  $\text{M-O-M}$  angles. Only small differences in  $\text{M-O-M}$  angle are needed to induce sizeable alterations in the chemical shift of the bridging oxygen. The decavanadate anion  $\text{V}_{10}\text{O}_{28}^{6-}$  contains three similar VOV bridges which have  $^{17}\text{O}$  chemical shifts of 766, 780 and 893 p.p.m.<sup>(168)</sup>

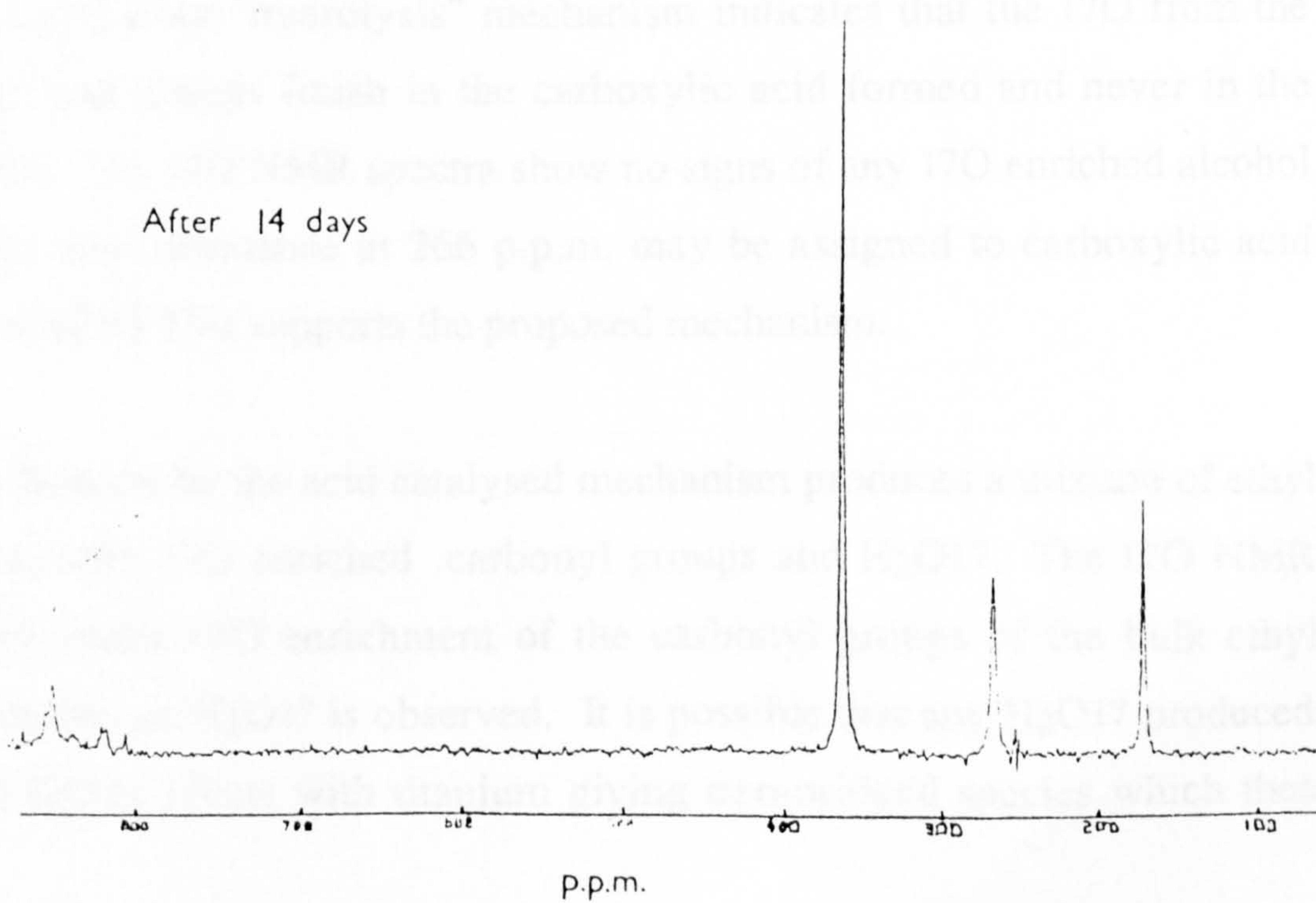
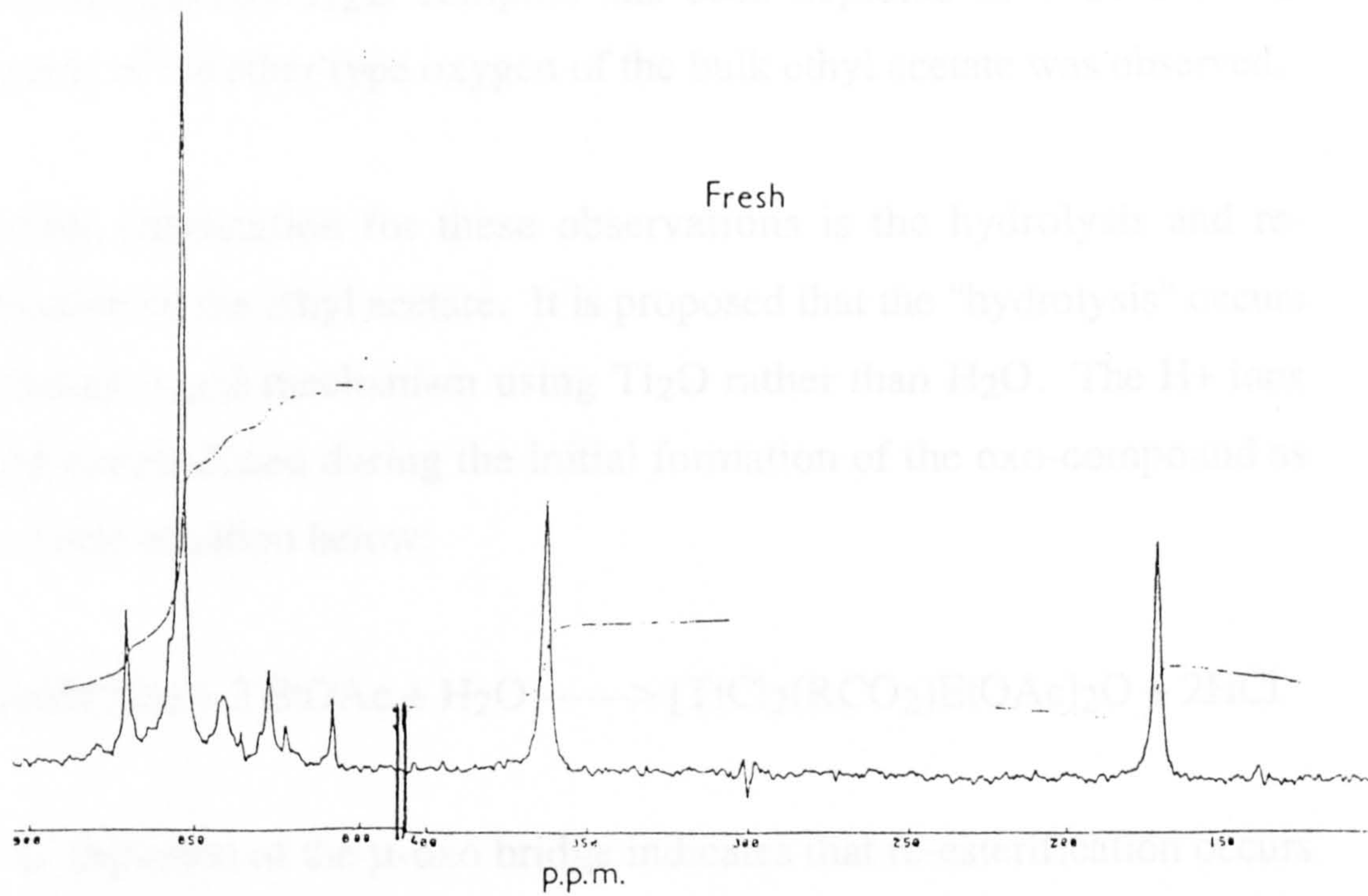
If the  $^{17}\text{O}$  NMR spectrum of the oxo-bridged complexes is remeasured after allowing the solutions to stand a number of changes are observed. The resonances due to the  $\mu$ -oxo oxygens have almost disappeared and a new resonance at 266 p.p.m. has appeared. The resonance at 363 p.p.m. due to the carbonyl oxygen of the ethyl acetate has increased in size relative to the resonance at 171 p.p.m. due to the ether type oxygen. These changes are shown in Figure 4.8.

TABLE 4.1      <sup>17</sup>O NMR SPECTRAL DATA FOR  
[TiCl<sub>2</sub>(RCO<sub>2</sub>)EtOAc]<sub>2</sub>O in EtOAc.

Compound	Chemical	Shifts	(p.p.m.)	[Intensity]
[TiCl <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> )EtOAc] <sub>2</sub> O	809 [22.4],	833 [4.9],	840 [4.9],	854[2.6]
{TiCl <sub>2</sub> [(CH <sub>3</sub> ) <sub>3</sub> CCO <sub>2</sub> ]EtOAc} <sub>2</sub> O	807 [4.3],	822 [2.7],	826 [6.2],	841 [4.6],
	853 [60.5],	870 [9.8].		



Figure 4.8  $^{17}\text{O}$  NMR Spectra of  $\{\text{TiCl}_2[(\text{CH}_3)_3\text{CCO}_2]\text{EtOAc}\}_2\text{O}$



The changes in the  $^{17}\text{O}$  NMR spectrum indicate the selective  $^{17}\text{O}$  enrichment of the carbonyl group of the bulk ethyl acetate and the production of  $^{17}\text{O}$  enriched carboxylic acid. The  $\mu$ -oxo bridge of the  $[\text{TiCl}_2(\text{RCO}_2)\text{EtOAc}]_2\text{O}$  complex has been depleted of  $^{17}\text{O}$ . No  $^{17}\text{O}$  enrichment of the ether type oxygen of the bulk ethyl acetate was observed.

A possible explanation for these observations is the hydrolysis and re-esterification of the ethyl acetate. It is proposed that the "hydrolysis" occurs by a variant  $\text{A}_{\text{AC}}2$  mechanism using  $\text{Ti}_2\text{O}$  rather than  $\text{H}_2\text{O}$ . The  $\text{H}^+$  ions required are produced during the initial formation of the oxo-compound as shown in the equation below:



The  $^{17}\text{O}$  depletion of the  $\mu$ -oxo bridge indicates that re-esterification occurs by the normal acid catalysed esterification mechanism. These mechanisms are shown in figures 4.9 and 4.10.

The  $\text{A}_{\text{AC}}2$  ester "hydrolysis" mechanism indicates that the  $^{17}\text{O}$  from the bridge will always finish in the carboxylic acid formed and never in the alcohol. The  $^{17}\text{O}$  NMR spectra show no signs of any  $^{17}\text{O}$  enriched alcohol but the new resonance at 266 p.p.m. may be assigned to carboxylic acid oxygens.<sup>(170)</sup> This supports the proposed mechanism.

Esterification by the acid catalysed mechanism produces a mixture of ethyl acetate with  $^{17}\text{O}$  enriched carbonyl groups and  $\text{H}_2\text{O}^{17}$ . The  $^{17}\text{O}$  NMR spectra show  $^{17}\text{O}$  enrichment of the carbonyl groups of the bulk ethyl acetate but no  $\text{H}_2\text{O}^{17}$  is observed. It is possible that any  $\text{H}_2\text{O}^{17}$  produced immediately reacts with titanium giving oxo-bridged species which then

take part in "hydrolysis" of the bulk ethyl acetate. As  $\text{H}^+$  is present any  $\text{H}_2\text{O}^{17}$  produced may take part in the acid catalysed hydrolysis of the bulk ethyl acetate.

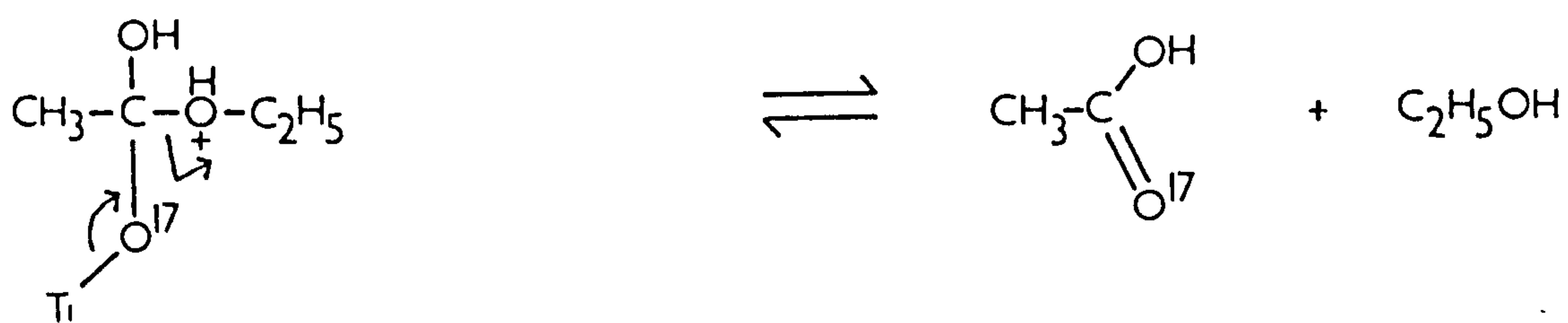
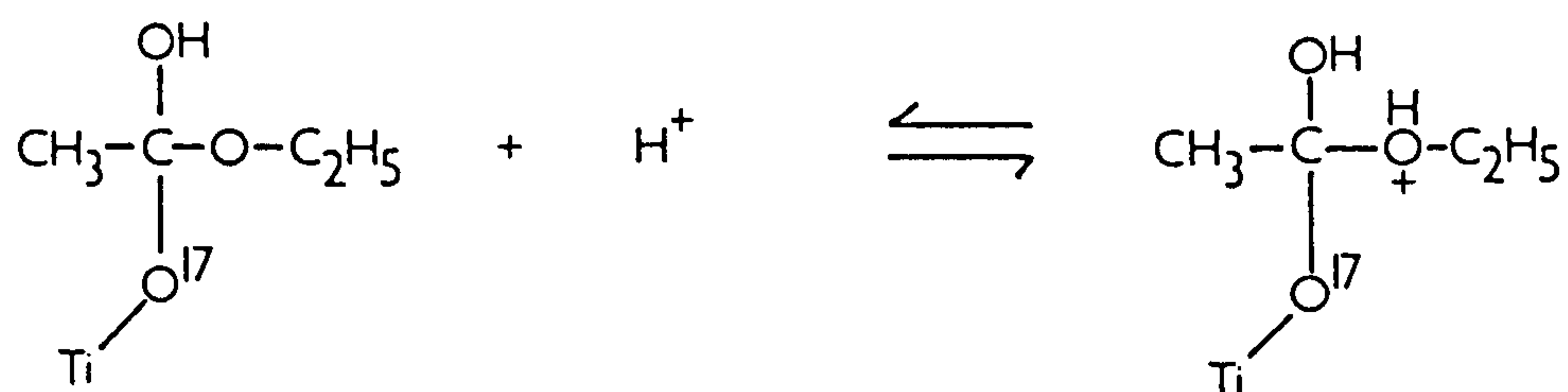
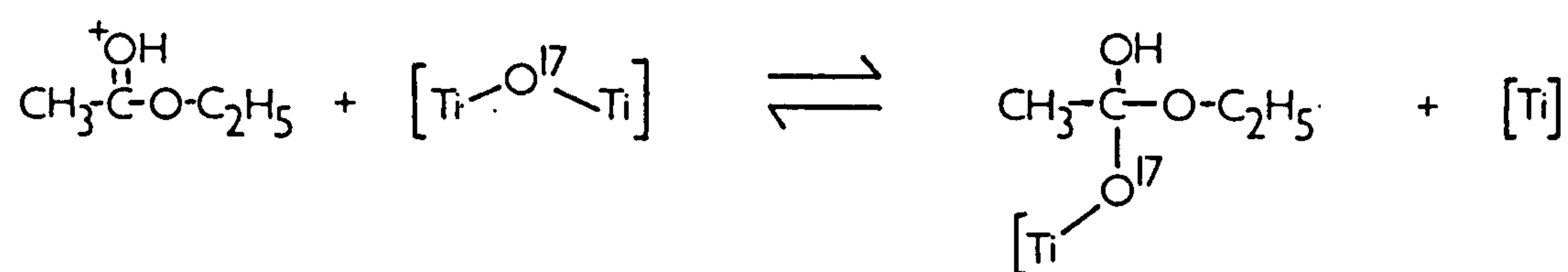
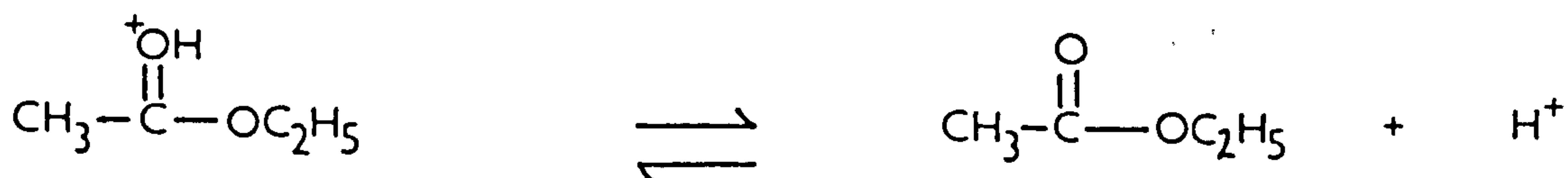
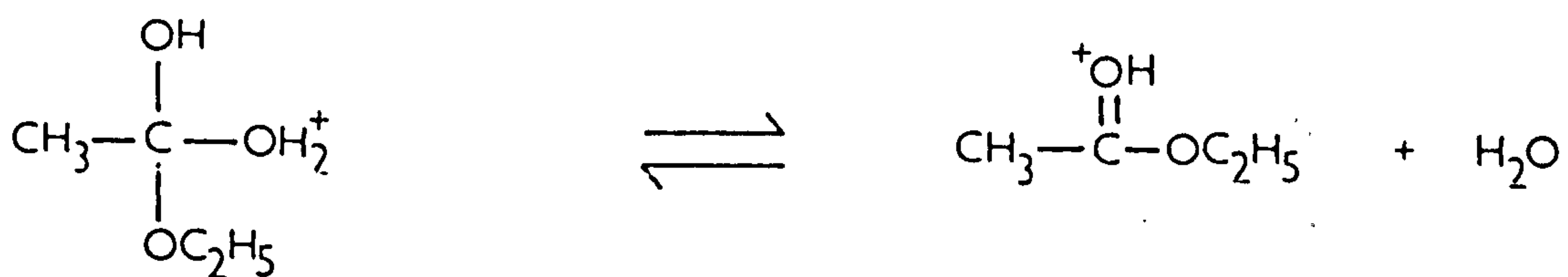
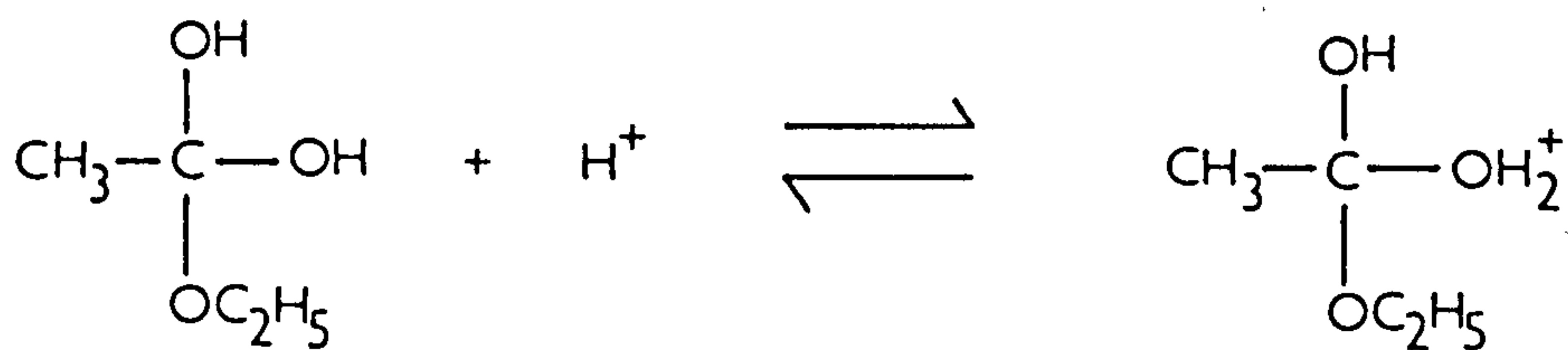
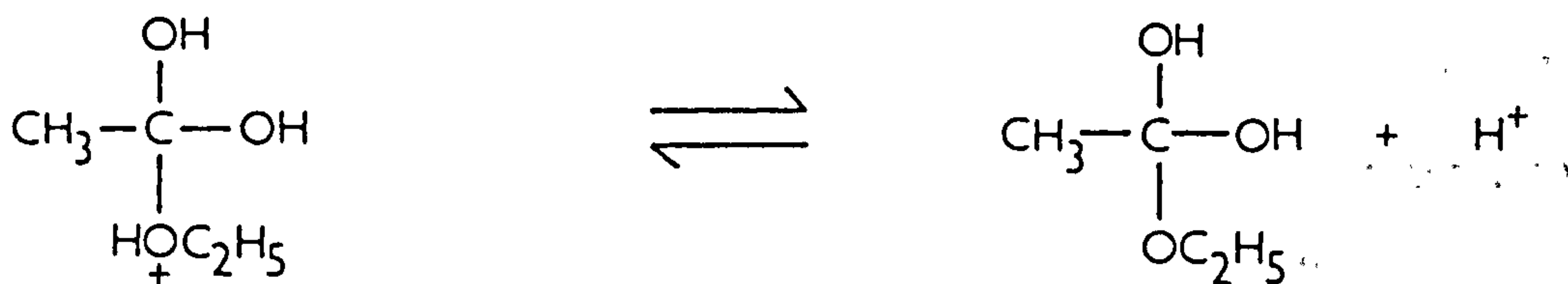
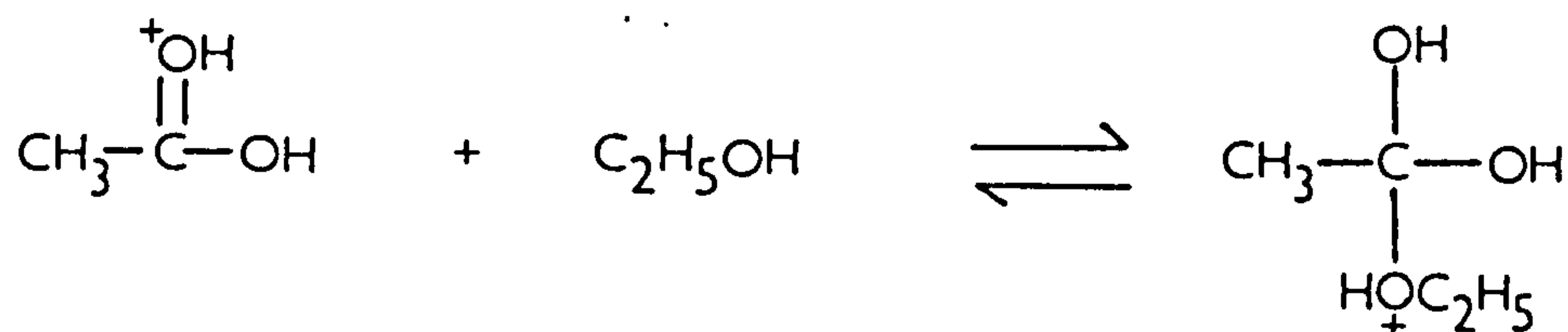
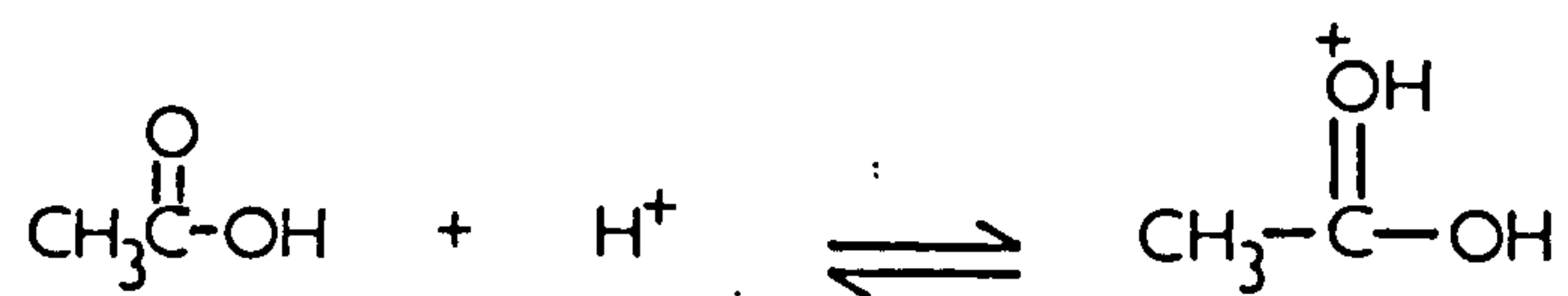
Figure 4.9. Modified A<sub>AC</sub>2 Ester Hydrolysis Mechanism



Figure 4.10. Acid Catalysed Esterification Mechanism



## **$^{17}\text{O}$ NMR Spectra of the 1 : 10 ( $\text{H}_2\text{O}/\text{Ti}$ ) Hydrolysis Product**

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  was dissolved in ethyl acetate which contained an appropriate quantity of  $\text{H}_2\text{O}^{17}$  to allow a large excess of titanium (1  $\text{H}_2\text{O}^{17}$  = 10 Ti). The  $^{17}\text{O}$  NMR spectrum of the solution was measured immediately and after allowing to stand for 7 days.

The spectra have resonances due to ethyl acetate at 162 and 172 p.p.m. These resonances have equal integrals. The other resonances of the spectra are reported in Table 4.2.

In both spectra the resonances around 800-900 p.p.m. are assigned to bidentate oxygens bridging two titanium atoms. The resonances at 266 p.p.m. and 247 p.p.m. are assigned to oxygens in a carboxylic acid. By comparison with vanadium (V) species<sup>(26)</sup> the resonances at 508 p.p.m. and 413 p.p.m. are tentatively assigned to triply bridging oxygen atoms.

On standing the resonances at 874 p.p.m., 853 p.p.m. and 847 p.p.m. disappear and the resonance at  $\sim 864$  p.p.m. diminishes in size. The ethyl acetate resonances at 362 p.p.m. and 172 p.p.m. remain equal in size. The resonances due to the triply bridging oxygens and the carboxylic acids increase in magnitude.

It seems that when a large excess of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  is hydrolysed by  $\text{H}_2\text{O}^{17}$  the carboxylate group is displaced and oxygen bridged species formed. The carboxylate may be displaced by  $\text{H}_2\text{O}^{17}$  attack upon the carboxyl groups carbon forming  $^{17}\text{O}$  enriched carboxylic acid or a  $^{17}\text{O}$  enriched Ti-O-Ti bridge. Some  $\text{H}_2\text{O}^{17}$  reacts with three titanium centres to give triply bridging oxygens.

On standing the bidentate bridged species are converted to the triply oxygen bridged complexes by the addition of another titanium. This process may involve displacement of a carboxylate as on standing the amount of  $^{17}\text{O}$  enriched carboxylic acid increases.

Finally the solution holds a small quantity of the most stable bidentate oxygen bridged species,  $^{17}\text{O}$  enriched carboxylic acid and one or more titanium complexes containing triply bridging oxygen atoms.

### Cyclic Voltammetry

The electrochemical properties of  $[\text{TiCl}_2(\text{RCO}_2)\text{L}]_2\text{O}$  were investigated by the cyclic voltammetry technique. The cyclic voltammogram of  $[\text{TiCl}_2(\text{C}_6\text{H}_5\text{CO}_2)\text{EtOAc}]_2\text{O}$  is shown in Figure 4.11.

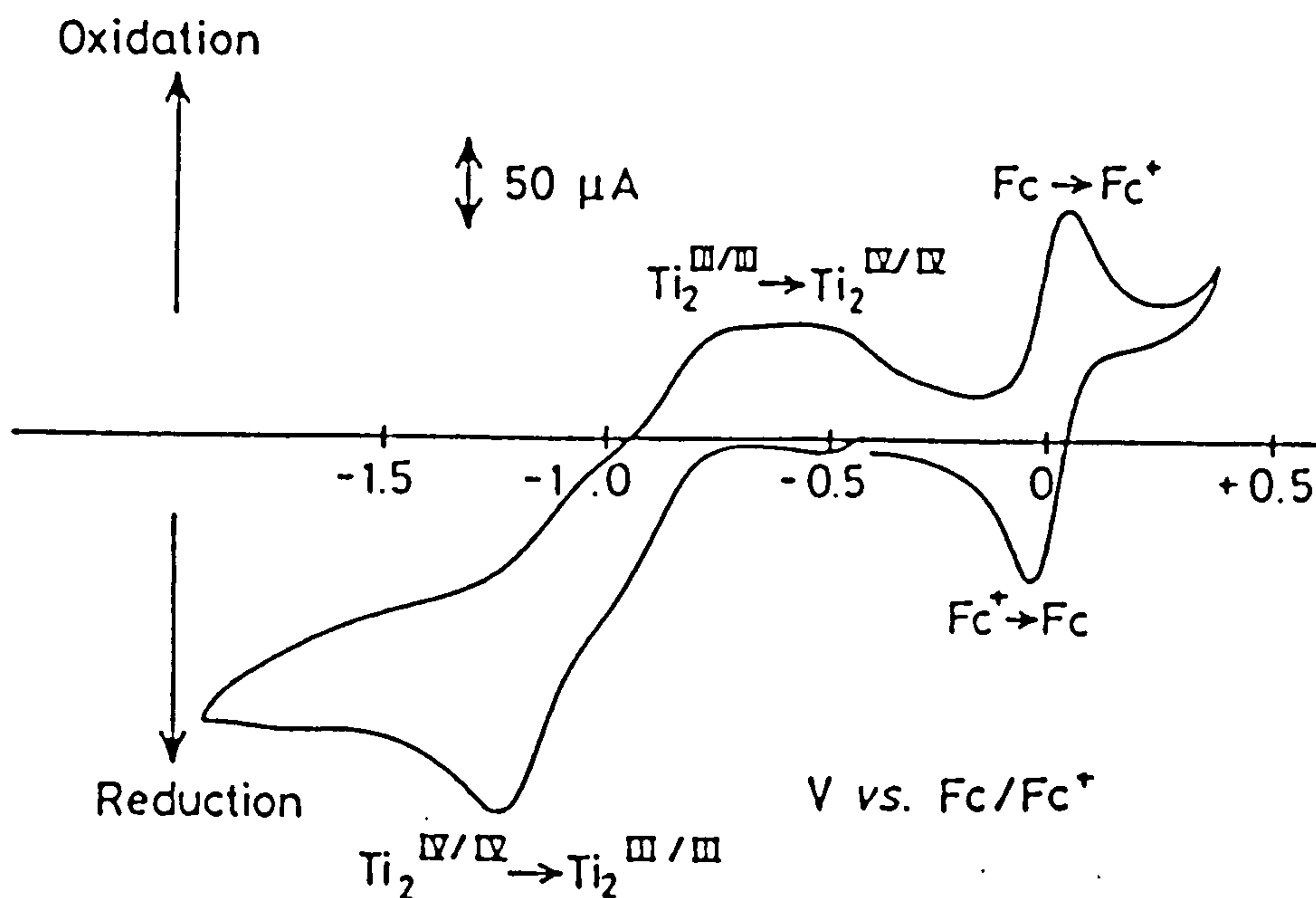


Figure 4.11. Cyclic voltammogram of  $[\text{TiCl}_2(\text{C}_6\text{H}_5\text{COO})\text{EtOAc}]_2\text{O}$

**Table 4.2    <sup>17</sup>O NMR Spectral Data for the 1:10 (H<sub>2</sub>O/Ti) Hydrolysis**

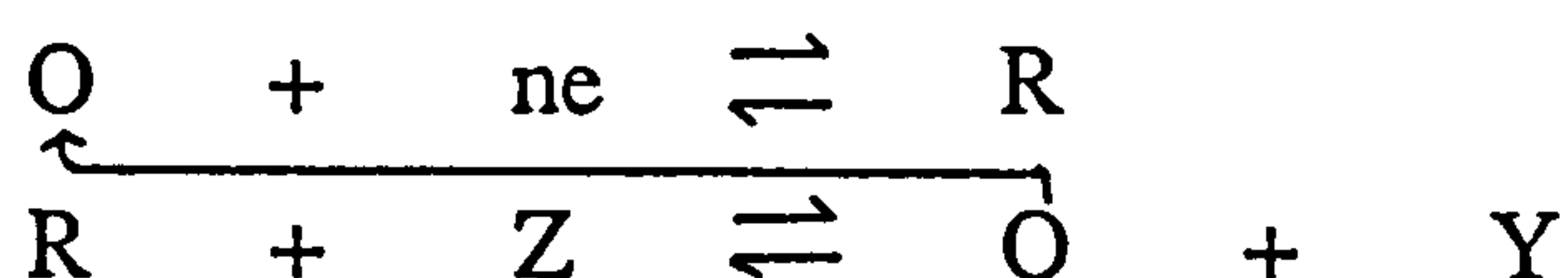
Time	Chemical Shifts      [Integral]				
Fresh	874 [9], 266 [68]	867 [38] 247 [35]	853 [8]	508 [38],	413 [24],
After 7 Days	864 [4]	504 [20]	409 [27]	263 [90]	247 [28]

<sup>a</sup> relative to H<sub>2</sub>O = 0.



The Voltammogram shows two one electron irreversible reduction waves at  $E_{p,c}$  -1.25 and -1.03V. There is a broad reoxidation wave at -0.65V. The measurements were made vs. ferrocenium (FC<sup>+</sup>) /ferrocene (FC) in dichloromethane with [<sup>n</sup>Bu<sub>4</sub>N][Cl] as the supporting electrolyte.

The value of  $i_{pa}/i_{pc}$  is approximately 1/2 indicating non-nernstian waves with an unstable reduction product.<sup>(171)</sup> An unstable reduction product is also indicated by the variation of peak height with sweep rate. There appears to be a reaction of the reduction product with a component of the solution which regenerates the starting material. This is an EC' mechanism as shown below:



O = species to be reduced, R = reduced species, Z = non-electroactive species, Y = side product.

The results indicate that both titanium (IV) centres are reduced to titanium (III).

It is noteworthy that the carboxylates  $\text{TiCl}_3(\text{RCO}_2)$  show no electrochemical activity within the solvent limits of dichloromethane.

These results may be compared with the electrochemical behavior of  $[\text{OsCl}_2(\text{CH}_3\text{CO}_2)\text{PPh}_3]_2\text{O}$ .<sup>(163)</sup> The complex undergoes a one electron reversible reduction with an  $E_{1/2}$  value of 0.18V and a one electron irreversible reduction with an  $E_{p,c}$  value of -0.93V. The ratio  $i_{pa}/i_{pc} \approx 1$  for sweep rates between 50 and 400 mV/s, the separation between the anodic

and cathodic peaks was 75mV. It was claimed that these properties indicate an electron transfer process which is reversible. No chemical reaction of the reduced product was observed.

## **CHAPTER 5**

### **TITANIUM - MAGNESIUM**

### **COMPLEXES**

## INTRODUCTION

The use of magnesium supported polymerisation catalysts has caused considerable interest in bimetallic complexes containing titanium and magnesium. There are many examples of effective polymerisation catalysts which use magnesium compounds as supports<sup>(2)</sup>. The components of a successful supported propylene polymerisation catalyst are limited. They are magnesium chloride, titanium tetrachloride and an aromatic ester used with triethylaluminium and another aromatic ester.

To obtain the required stereoregularity in the polymer produced the ester is complexed with the magnesium chloride and then reacted with the titanium tetrachloride<sup>(2)</sup>. A number of catalysts have been prepared by reaction of a magnesium chloride ester adduct with titanium tetrachloride<sup>(172)</sup>.

### Bimetallic Magnesium Complexes

Some complexes containing magnesium, titanium and an ester have been made. Giannini and coworkers prepared and structurally characterised  $\text{TiMgCl}_6(\text{CH}_3\text{COOC}_2\text{H}_5)_4$ . The magnesium and titanium centres are connected by a di- $\mu$ -chloro bridge. The titanium is octahedrally coordinated by six chlorine atoms and the magnesium octahedrally coordinated by the two bridging chlorine atoms and four carbonyl oxygen atoms of the  $\text{CH}_3\text{COOC}_2\text{H}_5$  ligands<sup>(11)</sup>. The complex is an effective polymerisation catalyst<sup>(172)</sup>. The structure of  $\text{TiMgCl}_6(\text{CH}_3\text{COOC}_2\text{H}_5)_4$  is shown in Figure 5.1:



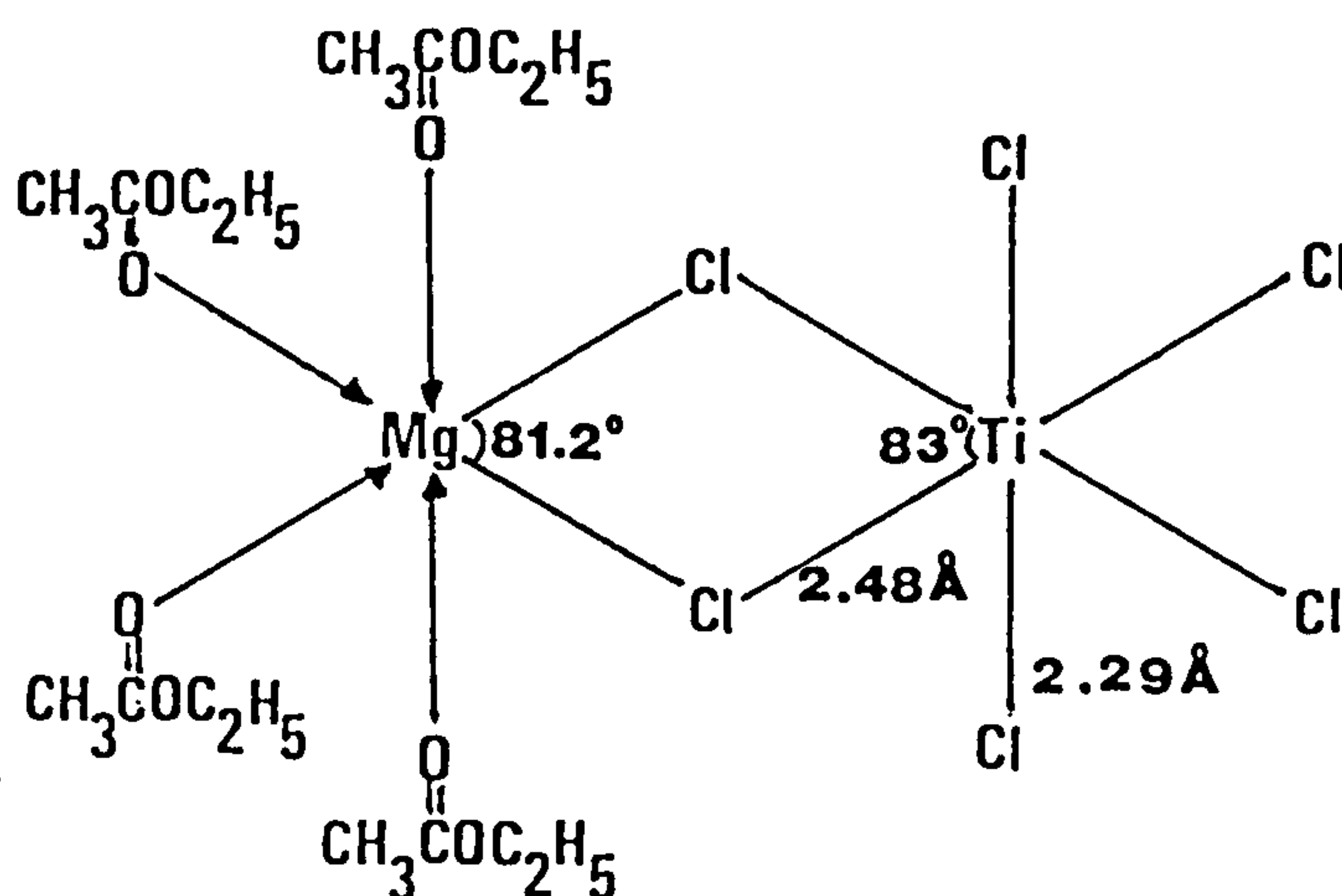


Figure 5.1. The Structure of  $\text{TiMgCl}_6(\text{CH}_3\text{COOC}_2\text{H}_5)_4$

The related complex  $\text{TiMgCl}_6(\text{THF})_4$  was prepared by the reaction of  $\text{TiCl}_4(\text{THF})_2$  and  $\text{MgCl}_2(\text{THF})_2$  in tetrahydrofuran<sup>(173)</sup> The complex is isostructural with  $\text{TiMgCl}_6(\text{EtOAc})_4$ .

When  $\text{TiCl}_4(\text{THF})_2$  and  $\text{MgCl}_2(\text{THF})_2$  are reacted in the ration 2 Mg : 1 Ti in tetrahydrofuran solution a different product is formed. The titanium compound removes  $\text{Cl}^-$  from bis (tetrahydrofuran) magnesium chloride to give the  $\text{TiCl}_5(\text{THF})^-$  anion. The  $[\text{MgCl}(\text{THF})_n]^+$  formed reacts with  $\text{MgCl}_2(\text{THF})_2$  to form the  $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$  cation<sup>(173)</sup> The X-ray crystal structure of the anion shows the titanium to be pseudo-octahedrally coordinated.<sup>(175)</sup> In the homobimetallic cation the two  $\text{Mg}^{2+}$  atoms are bridged by three chlorine atoms, the  $\text{Mg}^{2+}$  atoms achieve six coordination by bonding to three tetrahydrofuran molecules.<sup>(175)</sup> The structures of the cation and anion are shown in Figure 5.2:

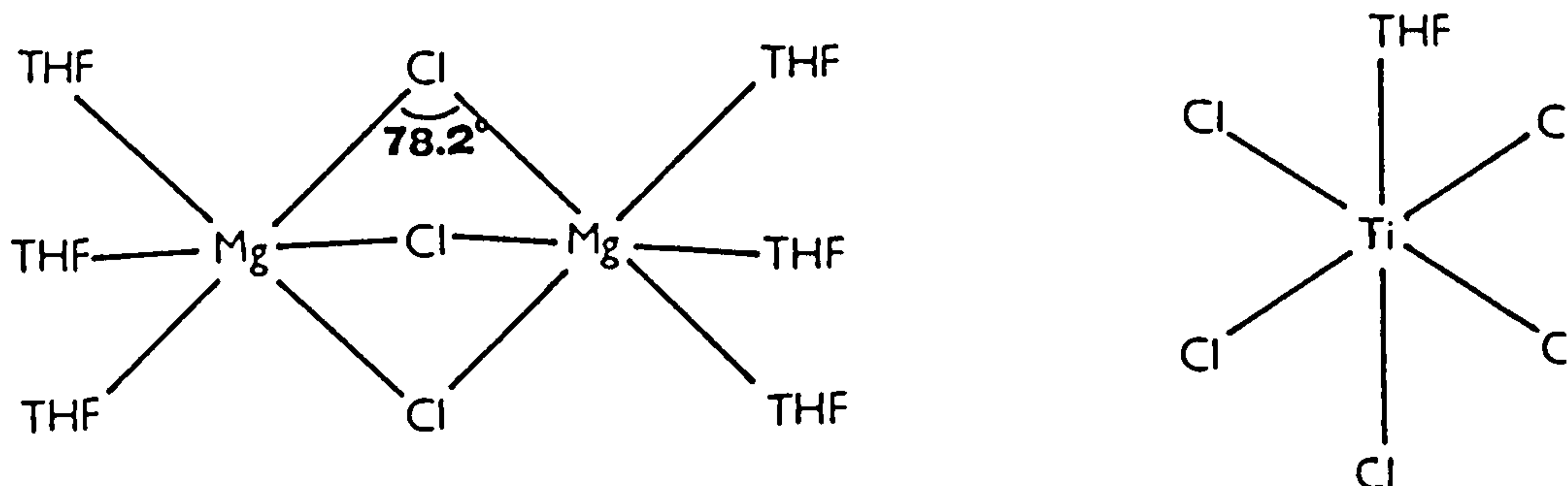


Figure 5.2. Structures of the  $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+$  cation and  $[\text{TiCl}_5(\text{THF})]^-$  anion.

The complexes (a)  $\text{MgCl}_2 \cdot \text{MCl}_4 \cdot 4\text{L}$  ( $\text{M} = \text{Ti}, \text{Zr}$  or  $\text{Sn}$ ;  $\text{L} = \text{CH}_3\text{COOC}_2\text{H}_5$  or  $\text{THF}$ ), (b)  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 4 \text{HCOOC}_2\text{H}_5$ , (c)  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 2 \text{CH}_3\text{COOC}_2\text{H}_5 \cdot 2\text{L}$  ( $\text{L} = \text{HCOOC}_2\text{H}_5$  or  $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$ ), (d)  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 2\text{CH}_3\text{COOC}_2\text{H}_5$  and (e)  $[(\text{MgCl}_2)_3 \cdot \text{TiCl}_4 \cdot (\text{SnCl}_4)_2 \cdot 12 \text{CH}_3\text{COOC}_2\text{H}_5]$  were prepared by Wallbridge and Gordon.<sup>(174)</sup> The ligand displacement reactions of the complexes were studied by  $^1\text{H}$  NMR spectroscopy showing that ethyl acetate is displaced by many other ligands. Preliminary X-ray structural studies on  $\text{MgCl}_2 \cdot \text{SnCl}_4 \cdot 4\text{EtOAc}$  indicate it is isomorphous with  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 4\text{EtOAc}$ .

Reaction of  $\text{MgCl}_2$  with  $\text{TiCl}_4$  in  $\text{ClCH}_2\text{COOC}_2\text{H}_5$  solution produces the complex  $\text{TiMgCl}_5(\text{ClCH}_2\text{CO}_2)(\text{ClCH}_2\text{COOC}_2\text{H}_5)_3$ <sup>(12)</sup> The magnesium and titanium atoms are bridged by two chlorine atoms and a  $\text{ClCH}_2\text{CO}_2^-$  residue. The  $\text{ClCH}_2\text{CO}_2^-$  bridge comes from an ethylchloroacetate molecule which has lost an ethyl forming a carboxylate bridge. The infrared spectrum of the complex has two bands, at  $1620\text{cm}^{-1}$  and  $1325\text{cm}^{-1}$  which were assigned to  $\nu(\text{CO}_2^-)$  vibrations. The structure of  $\text{TiMgCl}_5(\text{ClCH}_2\text{CO}_2)(\text{ClCH}_2\text{COOC}_2\text{H}_5)_3$  is shown in Figure 5.3:

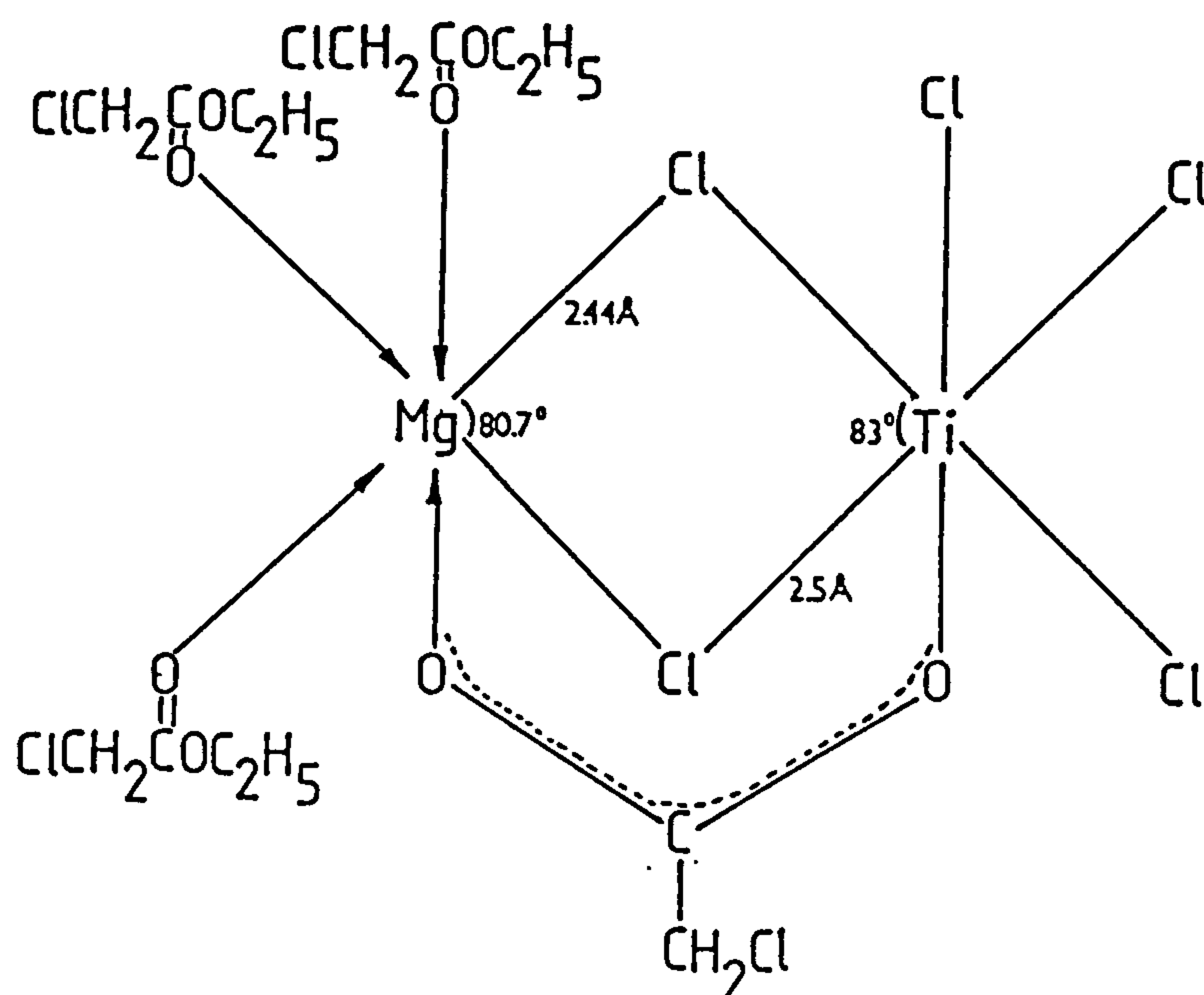


Figure 5.3. The Structure of  $\text{MgTiCl}_5(\text{ClCH}_2\text{CO}_2)(\text{ClCH}_2\text{COOC}_2\text{H}_5)_3$

Another complex containing a transition metal and magnesium joined by chlorine bridges was made by the reaction of ferric chloride and  $\text{MgCl}_2(\text{THF})_2$  in tetrahydrofuran. This produced the unstable complex  $[\text{MgCl}(\text{THF})_5][\text{FeCl}_4]$ .<sup>(176)</sup> The presence of  $[\text{FeCl}_4]^-$  was confirmed by addition of  $\text{Bu}_4\text{N}^+$  which gave the previously characterised compound  $[\text{Bu}_4\text{N}][\text{FeCl}_4]$ . The  $[\text{MgCl}(\text{THF})_5][\text{FeCl}_4]$  was unstable in solution changing to the chloro-bridged complex  $[\text{FeCl}_2(\mu\text{-Cl})_2\text{Mg}(\text{THF})_4]$ . It was claimed that the reduction of the iron was caused by cleavage of tetrahydrofuran. The X-ray crystal structure of  $[\text{FeCl}_2(\mu\text{-Cl})_2\text{Mg}(\text{THF})_4]$  shows a distorted tetrahedral geometry for the iron (II) atom and distorted octahedral geometry for the Mg(II) atom. The structure of  $[\text{FeCl}_2(\mu\text{-Cl})_2\text{Mg}(\text{THF})_4]$  is shown in figure 5.4:



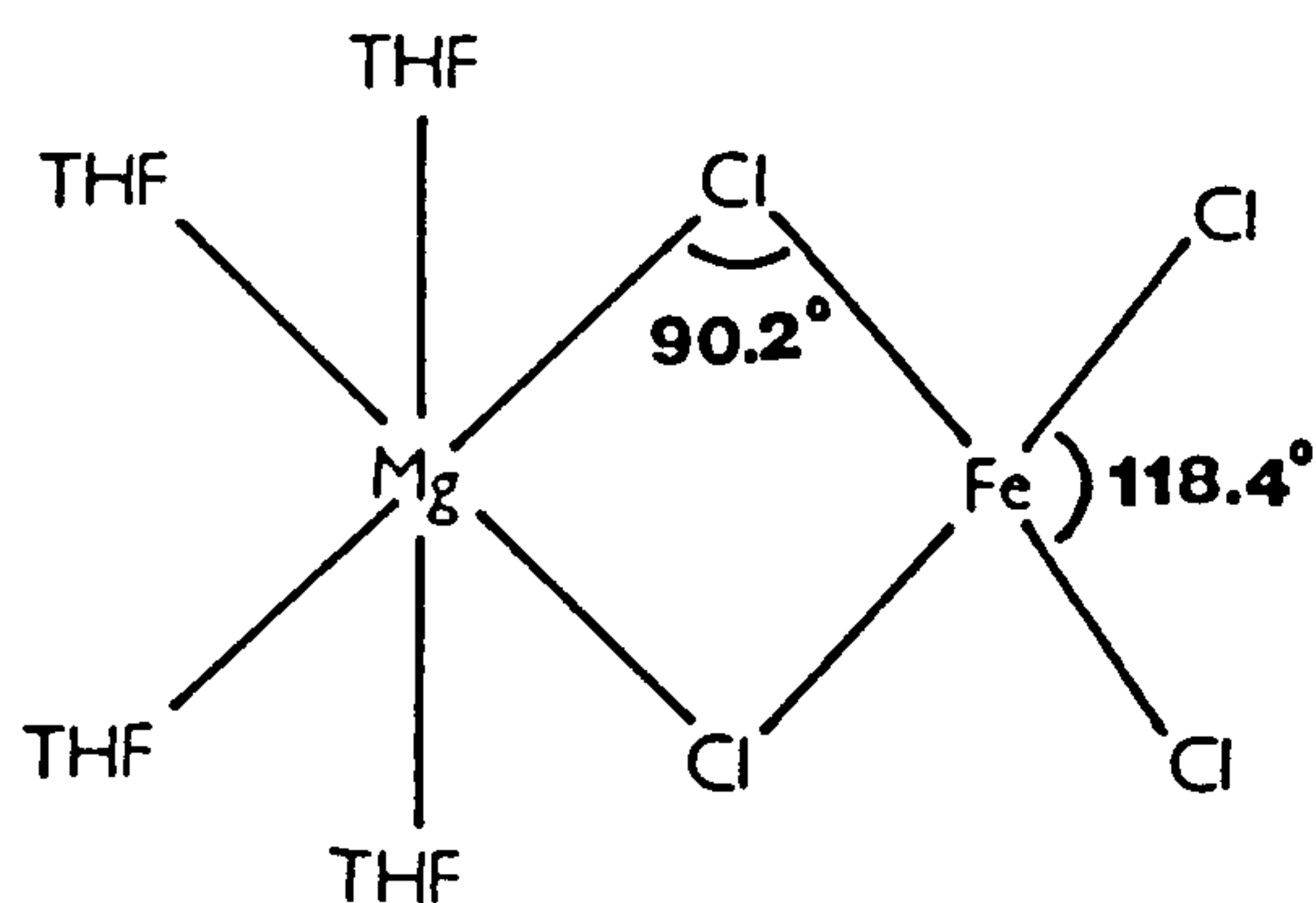


Figure 5.4. The structure of  $\text{FeMgCl}_4(\text{THF})_4$

### Preparation and Properties of Bimetallic Titanium-Magnesium Complexes.

A number of different methods were used in attempts to prepare titanium-magnesium bimetallic complexes. The aim of the experiments was to make a bimetallic complex with the metal centres joined by carboxylate bridges as in the compound  $\text{TiMgCl}_5(\text{ClCH}_2\text{CO}_2)(\text{ClCH}_2\text{COOC}_2\text{H}_5)_3$  (12)

Magnesium carboxylates were reacted with titanium tetrachloride in chloroform or ethyl acetate solution. No reaction occurred in chloroform, unreacted  $\text{Mg}(\text{CH}_3\text{CO}_2)_2$  was recovered from the reaction mixture. Reaction of magnesium benzoate with titanium tetrachloride in ethyl acetate produced a yellow solid which was recrystallised from dichloromethane/hexane.

The  $^1\text{H}$  NMR spectrum of the yellow solid showed that  $\text{C}_6\text{H}_5\text{CO}_2^-$  and ethyl acetate residues were present in a 1:1 ratio. The infra-red spectrum of the solid contained bands due to Ti-Cl stretching vibrations as well as bands due



to ethyl acetate and the benzoate carboxyl group. Elemental analyses indicated that the solid was  $\text{TiMgCl}_4(\text{C}_6\text{H}_5\text{CO}_2)_2(\text{CH}_3\text{COOC}_2\text{H}_5)_2$ .

The reaction of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with magnesium oxide in ethyl acetate solution forms a pale yellow solid. Infra-red and  $^1\text{H}$  NMR spectra show the presence of both ethyl acetate and pivalate residues. The elemental analysis of the solid shows it to be a mixture of the titanium (IV) pivalate ethyl acetate adduct and magnesium oxide.

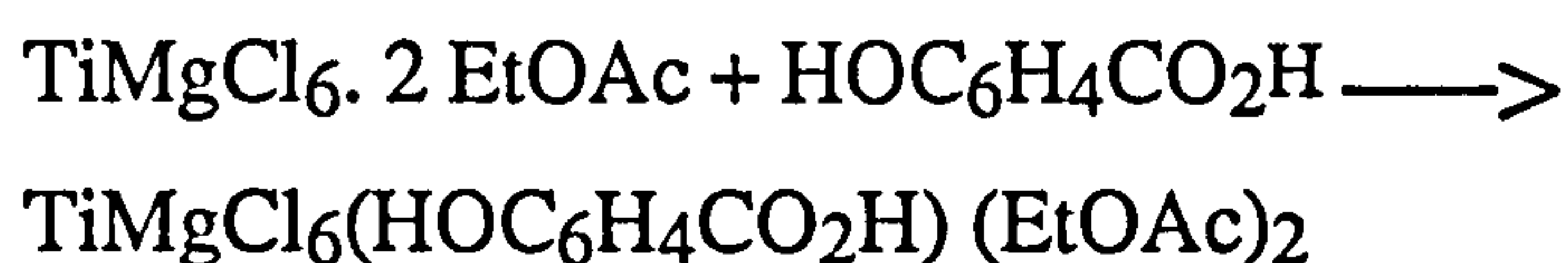
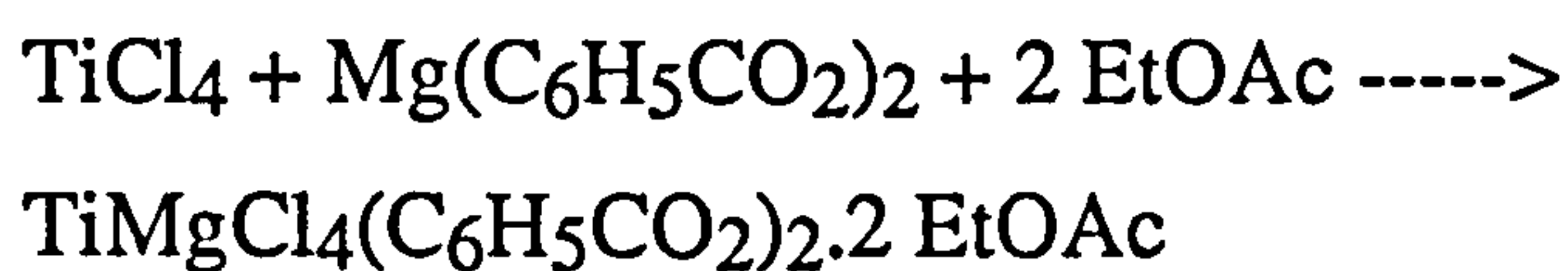
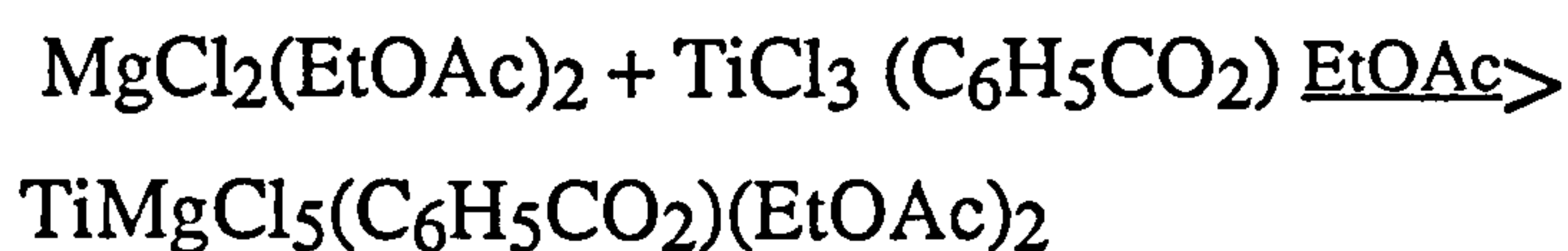
A standard solution of magnesium chloride in ethyl acetate was prepared by refluxing a mixture of  $\text{MgCl}_2$  and EtOAc for eighteen hours. The reaction of this standard solution with titanium tetrachloride,  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2\text{H}$  and THF gave a yellow solid. The solid was recrystallised from dichloromethane giving small yellow crystals. When the solid was analysed it was found to contain no magnesium.

The  $\text{MgCl}_2$  solution was reacted with a solution of  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$  in ethyl acetate. This gave a yellow solid which turns greenish yellow upon heating. The infra-red spectrum of the solid contains bands due to  $\nu(\text{CO}_2^-)$  vibrations, ethyl acetate and Ti-Cl vibrations. The  $^1\text{H}$  NMR spectrum of the solid has resonances at 8.2 p.p.m., 7.55 p.p.m., 4.4 p.p.m., 2.35 p.p.m., and 1.35 p.p.m. The resonances at 8.2 and 7.55 p.p.m. are assigned to ring protons of the benzoate residue. The resonances at 4.4, 2.35 and 1.35 p.p.m. are due to coordinated ethyl acetate. The titanium and magnesium analyses of the product indicated that it has a formulation as  $\text{TiMgCl}_5(\text{C}_6\text{H}_5\text{CO}_2)(\text{EtOAc})_2$ .

The complex  $\text{TiMgCl}_6 \cdot 2\text{CH}_3\text{COOC}_2\text{H}_5$  was prepared by the method described by Giannini.<sup>(172)</sup> Reaction of this complex with para-

hydroxybenzoic acid in ethyl acetate gave an immediate precipitate of an orange solid. The solid was insoluble in all common organic solvents. The infra-red spectrum of the solid has a band due to the carbonyl group of ethyl acetate at  $1680\text{cm}^{-1}$  implying that the ester is coordinated to magnesium. Bands due to  $\nu(\text{CO}_2^-)$  and metal-halogen modes are also observed. A band at  $3390\text{cm}^{-1}$  is assigned to the hydroxyl group of the para-hydroxybenzoic acid residue. Titanium and magnesium analyses indicate the orange solid is  $\text{TiMgCl}_6(\text{HOC}_6\text{H}_4\text{CO}_2\text{H})(\text{EtOAc})_2$ . A proposed structure for  $\text{TiMgCl}_6(\text{RCO}_2\text{H})_2 \cdot 2 \text{EtOAc}$  compounds is shown in Figure 5.5.

Some equations for the reactions forming these compounds are shown below:



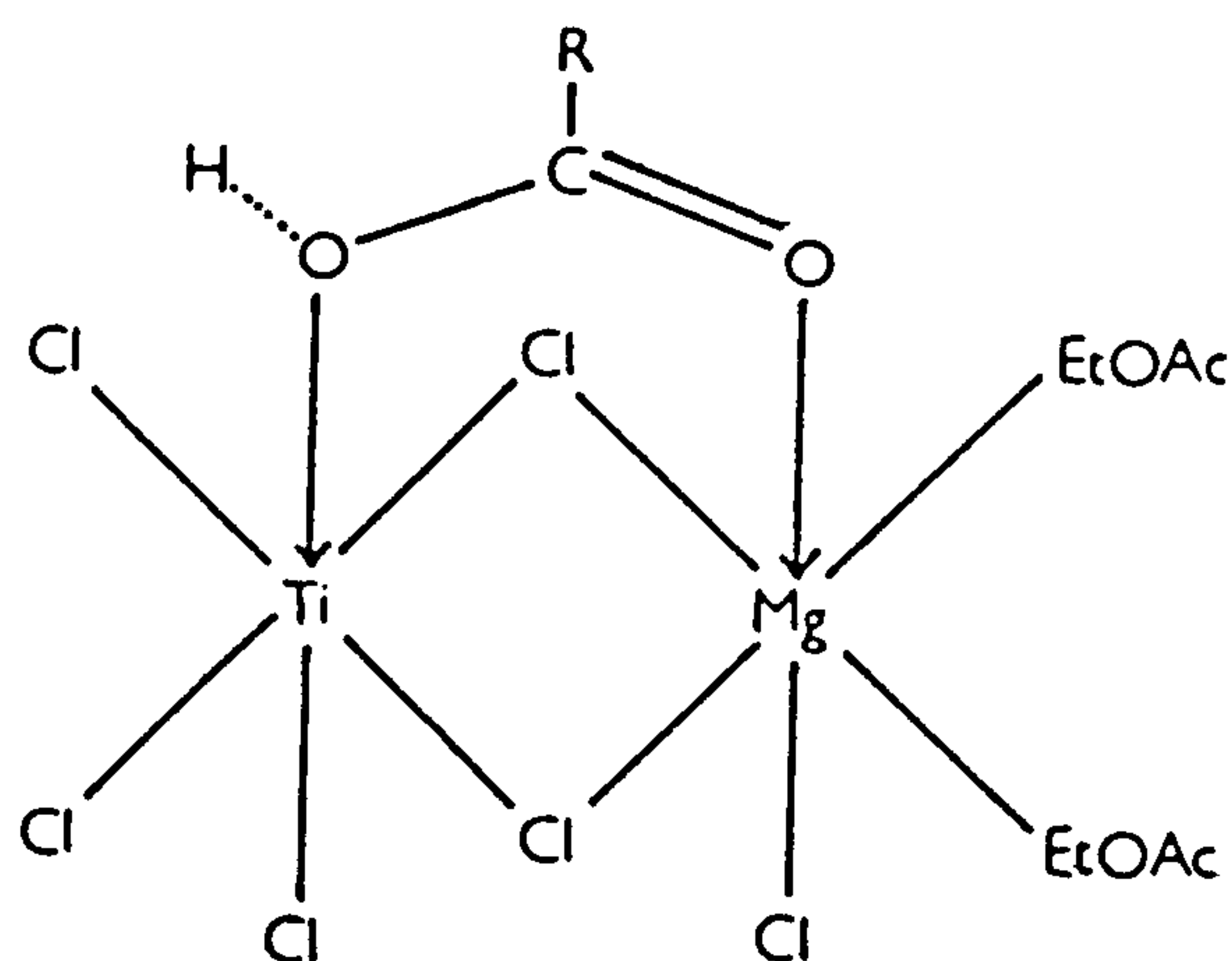


Figure 5.5. General Structure for  $\text{TiMgCl}_6(\text{RCO}_2\text{H})(\text{EtOAc})_2$   
Complexes

## Discussion

Gianni and coworkers claim in a Montedison SpA patent to have prepared the complex  $\text{TiMgCl}_5(\text{C}_6\text{H}_5\text{CO}_2) \cdot 2\text{EtOAc}$  (172). The complex was prepared by reaction of  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$  with an ethyl acetate solution of anhydrous  $\text{MgCl}_2$ . The compound is reported to be green.

The yellow complex  $\text{TiMgCl}_5(\text{C}_6\text{H}_5\text{CO}_2) \cdot 2\text{EtOAc}$  prepared during our investigations turns green upon heating. It is possible that it is converted to green  $\text{TiMgCl}_5(\text{C}_6\text{H}_5\text{CO}_2) \cdot 2\text{EtOAc}$  by the action of heat. The similar compound  $\text{TiMgCl}_6(\text{HOC}_6\text{H}_4\text{CO}_2\text{H}) \cdot 2\text{EtOAc}$  does not change colour upon heating. The extreme insolubility of the complex suggests it is polymeric.

In the complex  $\text{TiMgCl}_4(\text{C}_6\text{H}_5\text{CO}_2)_2 (\text{EtOAc})_2$  the titanium and magnesium atoms may be linked by both chlorine and carboxylate bridges. The ethyl acetate is probably coordinated to magnesium as previous studies have shown magnesium is the preferred coordination centre for ethyl



acetate<sup>(174)</sup> A possible structure for  $\text{TiMgCl}_4(\text{C}_6\text{H}_5\text{CO}_2)_2 \cdot 2\text{EtOAc}$  is shown in Figure 5.6:

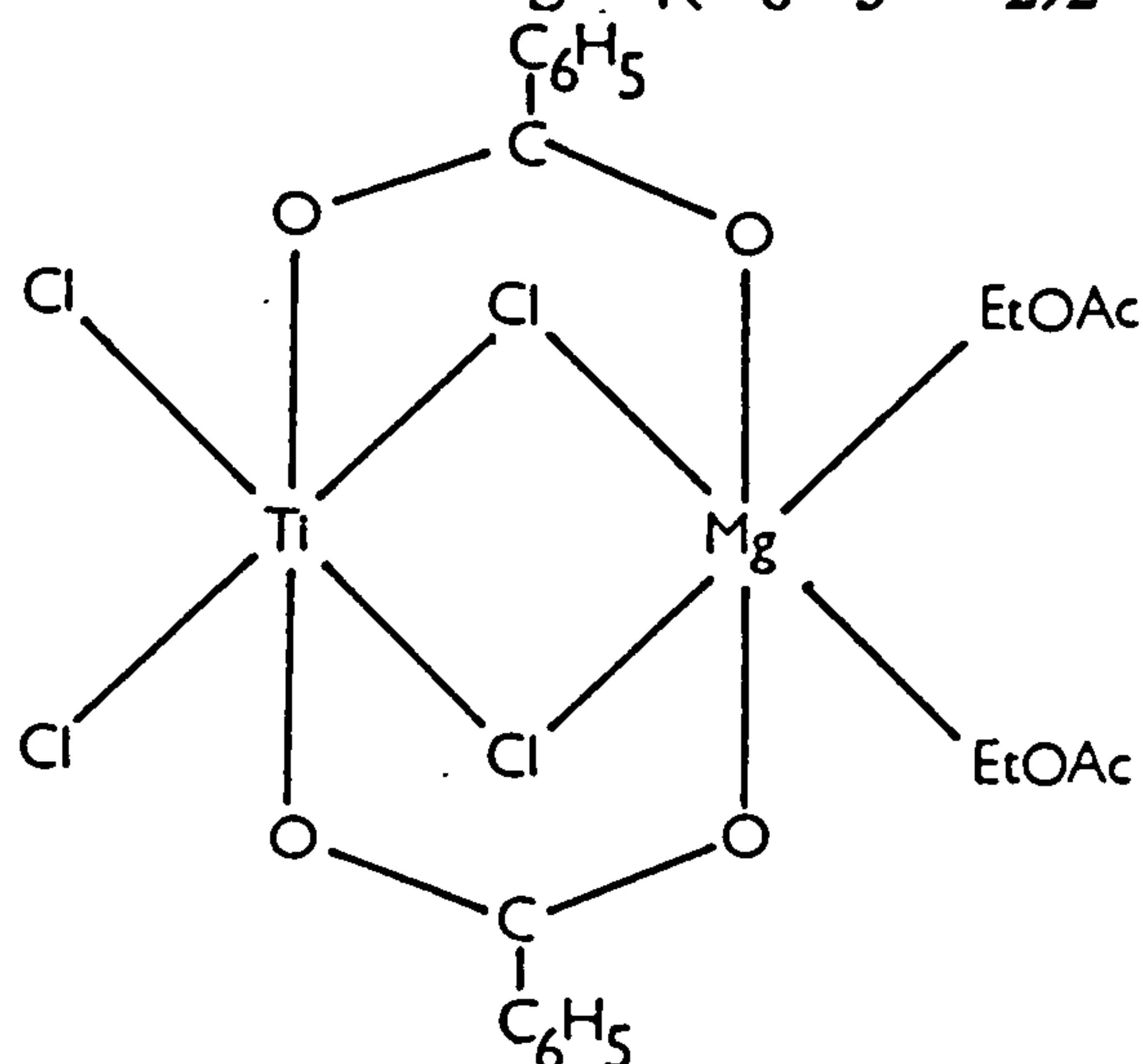


Figure 5.6. A Possible Structure for  $\text{TiMgCl}_4(\text{C}_6\text{H}_5\text{CO}_2)_2 \cdot 2\text{EtOAc}$

These and previous studies<sup>(173,174,176)</sup> have shown that magnesium chloride will only react with titanium compounds when it is present as a solvate. The magnesium chloride solvates are prepared using coordinating solvents such as ethyl acetate or tetrahydrofuran. The solvates  $\text{MgCl}_2(\text{THF})_2$  and  $\text{MgCl}_2(\text{THF})_4$  have been investigated by Handiv and coworkers<sup>(177)</sup>

The unreactivity of anhydrous magnesium chloride is probably due to its highly crystalline nature. Magnesium chloride has a  $\text{CdCl}_2$  type layer lattice structure each magnesium being surrounded by six chlorine atoms. The coordinating solvent may break up the lattice increasing the surface area of the magnesium chloride and making it more vulnerable to attack by titanium.



# **CHAPTER 6**

## **EXPERIMENTAL**

## EXPERIMENTAL

Almost all of the compounds which have been studied in this thesis are oxygen and/or moisture sensitive and so had to be manipulated in an atmosphere of dry, inert nitrogen gas. Crystals for X-ray diffraction were handled in argon gas. The compounds were prepared and manipulated using standard Schlenk techniques<sup>(178,179)</sup> and a nitrogen filled glovebox<sup>(180)</sup> When required solvents and reagents were purified and dried by the methods described in the next section.

### Purification and drying of reagents and solvents

#### Acetylacetone

Acetylacetone was supplied by Fisons Ltd. It was distilled from  $\text{NaHCO}_3$  and  $\text{P}_2\text{O}_5$  prior to use.

#### Aromatic Solvents

Benzene and toluene were supplied by Fisons Ltd. Both were stored over Na wire. Benzene was distilled from  $\text{CaH}_2$  before use. Toluene was distilled from Na benzophenone ketal before use.

#### Carboxylic Acids

Crotonic, 2,2-diphenylpropionic, p-hydroxybenzoic, pivalic and 2,4,6 - Trimethyl-benzoic acids were supplied by Aldrich Ltd. 2,2-Diphenyl-propionic acid was recrystallised from  $\text{CH}_2\text{Cl}_2$  before use. Benzoic acid was supplied by May and Baker Ltd., isobutyric and cinnamic acids were

supplied by B.D.H. Ltd. All isomers of toluic acid were supplied by Fisons Ltd. Isobutyric acid was distilled from  $P_2O_5$  before use. The other acids were used without further purification.

### Chlorinated Solvents

$CH_2Cl_2$ ,  $CHCl_3$  and  $CCl_4$  were supplied by Fisons Ltd. Chlorobenzene was supplied by Aldrich Ltd.  $CHCl_3$ ,  $CCl_4$  and  $C_6H_5Cl$  were distilled from  $CaCl_2$  prior to use.  $CH_2Cl_2$  was distilled from  $CaH_2$  before use.

### Dibenzoyl Methane

$C_6H_5COCH_2COC_6H_5$  was supplied by Aldrich Ltd. and used without further purification.

### Diethyl Ether

$Et_2O$  was supplied by May & Baker Ltd. It was stored over Na wire and distilled from Na/benzophenone ketal before use.

### Ethyl Acetate

$CH_3COOC_2H_5$  was supplied by Fisons Ltd. It was shaken with  $NaHCO_3$  and distilled from  $CaH_2$  before use.

### Hexane

Hexane was supplied by Fisons Ltd. and distilled from  $CaH_2$  prior to use.

## Metal Chlorides

Anhydrous  $\text{MgCl}_2$  was supplied by I.C.I. Plc and was not purified further before use.

$\text{TiCl}_4$  was supplied by B.D.H. Ltd. and was not purified further before use.

## Magnesium Oxide

$\text{MgO}$  was supplied by May and Baker Ltd., and was not purified further before use.

## Petroleum Ethers

Petroleum ether (B.P. 60-80°C) was supplied by B.D.H. Ltd. Petroleum ether (B.P. 100-120°C) was supplied by Fisons Ltd. Both were distilled from  $\text{CaH}_2$  prior to use. Unless otherwise stated all petroleum ether used was B.P. 60-80°C.

## Pyridine

$\text{C}_5\text{H}_5\text{N}$  was supplied by Fisons Ltd. It was dried over solid  $\text{KOH}$  and distilled onto 3A molecular sieves before use.

## Tetrahydrofuran

$\text{C}_4\text{H}_8\text{O}$  was supplied by May and Baker Ltd. It was distilled from  $\text{Na}$ /benzophenone Ketal before use.



## Titanium Alkoxides

$\text{Ti}(\text{OPr}^i)_4$  was supplied by Bentron GMBH and used without further purification.

## Preparation and Reactions of Titanium (IV)

### Trischloromonocarboxylates

#### Preparation of $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$

$\text{TiCl}_4$  (5.5 cm<sup>3</sup>, 50.16 mmol) was added dropwise to a magnetically stirred solution of  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$  (5.375 g, 44.06 mmol) in toluene (60 cm<sup>3</sup>). A yellow precipitate formed immediately, which dissolved to form a dark red solution when the suspension was heated to 100°C for 1 hour. On cooling to room temperature an orange precipitate formed. The supernatant liquid was removed and the solid washed with petroleum ether (2 x 40 cm<sup>3</sup>). It was then dried in *vacuo* for 7 hours. (Yield 11.05 g, 91%).

i.r.	1600(s)	1555(s)	1500(s)	1460(s)	1410(m)
	1380(s)	1315(m)	1180(m)	1160(s)	1100(m)
	1070(w)	1025(m)	1000(w)	850(w)	800(m)
	750(s)	690(s)	570(m)	640(m)	620(s)
	570(s)	510(s)	410(s)	375(s)	320(m)
	290(w)	260(m)	cm-1		

<sup>1</sup>H NMR 7.5-8.5(m) p.p.m.

Analysis for  $\text{TiCl}_3\text{C}_7\text{H}_5\text{O}_2$ :

	Ti	Cl
Calculated:	17.39	38.67 %
Found:	17.43	38.51 %

### Preparation of $\text{TiCl}_3[\text{CH}_3\text{C}(\text{C}_6\text{H}_5)_2\text{CO}_2]$

$\text{TiCl}_4$  ( $1.5\text{cm}^3$ ,  $13.68\text{mmol}$ ) was added slowly to a magnetically stirred solution of  $\text{CH}_3\text{C}(\text{C}_6\text{H}_5)_2\text{CO}_2\text{H}$  ( $2.84\text{g}$ ,  $12.57\text{mmol}$ ) in benzene ( $30\text{cm}^3$ ). The resulting red solution was stirred for 4 hours and pumped to dryness forming an orange solid. The solid was washed with petroleum ether ( $4 \times 20\text{cm}^3$ ) and dried in *vacuo* for 3 hours. (Yield  $2.63\text{g}$ ,  $55\%$ ).

i.r.	1645(m)	1600(m)	1530(s)	1490(m)	1225(m)
	1190(w)	1160(w)	1125(m)	1105(w)	1080(m)
	1065(w)	1030(m)	1000(w)	865(sh)	790(sh)
	760(m)	700(s)	660(m)	630(b)	530(m)
	470(m)	420(m)	385(m)	330(sh)	$\text{cm}^{-1}$

$^1\text{H}$  NMR 7.0-7.4(m) (10H), 1.74(s) (3H) p.p.m.

Analysis for  $\text{TiCl}_3\text{C}_{15}\text{H}_{13}\text{O}_2$ :

**Ti**

Calculated: 12.62 %

Found: 12.52 %

### Preparation of $\text{TiCl}_3[(\text{CH}_3)_2\text{CHCO}_2]$

$\text{TiCl}_4$  ( $3.6\text{cm}^3$ ,  $32.83\text{mmol}$ ) was added slowly to a magnetically stirred solution of  $(\text{CH}_3)_2\text{CHCO}_2\text{H}$  ( $2.7\text{cm}^3$ ,  $29.67\text{mmol}$ ) in  $\text{CCl}_4$  ( $30\text{cm}^3$ ). A yellow precipitate formed immediately. The suspension was stirred for 12 hours and pumped to dryness. The resulting yellow foam was recrystallised from  $\text{CCl}_4$  ( $10\text{cm}^3$ ) to form a yellow powder. The powder was washed with

petroleum ether (3x30cm<sup>3</sup>) and dried in *vacuo* for 3 hours. (Yield 2.29g, 32%).

i.r.	1650(b)	1600(m)	1500(sh)	1360(m)	1300(m)
	1170(m)	1100(m)	1030(m)	945(m)	745(m)
	675(w)	580(sh)	390(s)	320(m)	cm <sup>-1</sup>

<sup>1</sup>H NMR 2.23(s) (1H), 0.8-1.2(ms) (6H) p.p.m.

Analysis for TiCl<sub>3</sub>C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>:

	Ti
Calculated:	19.84 %
Found:	20.31 %

### Attempted Preparations of TiCl<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CO<sub>2</sub>)

- (i) TiCl<sub>4</sub> (2.4cm<sup>3</sup>, 21.89mmol) was added slowly to a solution of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CO<sub>2</sub>H (2.38g, 17.5mmol) in benzene (30cm<sup>3</sup>). The resulting red solution was stirred for an hour and the volume of solvent reduced by pumping. The addition of petroleum ether (50cm<sup>3</sup>) (in order to precipitate the product) produced an intractable red oil.
- (ii) TiCl<sub>4</sub> (3.3cm<sup>3</sup>, 30mmol) was added slowly to a solution of C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>H (3.31g, 24.34mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15cm<sup>3</sup>). The resulting orange solution was stirred for 8 hours and the volume of solvent reduced by pumping. An orange solid precipitated from the solution. It was washed with petroleum ether (3x30cm<sup>3</sup>) and dried in *vacuo* for 3 hours. After 8 hours the orange solid had turned black.



in vacuo for 3 hours. After 8 hours the orange solid had turned black.

- (iii)  $\text{TiCl}_4$  ( $1.8\text{cm}^3$ ,  $16.42\text{mmol}$ ) was added slowly to a solution of  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$  ( $2.177\text{g}$ ,  $16.00\text{mmol}$ ) in  $\text{Et}_2\text{O}$  ( $30\text{cm}^3$ ) at  $-78^\circ\text{C}$ . A yellow precipitate formed immediately along with some orange solid. The supernatant liquid was removed and the solid washed with petroleum ether ( $2 \times 20\text{cm}^3$ ). The yellow and orange solids then turned green.
- (iv)  $\text{TiCl}_4$  ( $2\text{cm}^3$ ,  $18.24\text{mmol}$ ) was added slowly to a solution of  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$  ( $2.18\text{g}$ ,  $16.03\text{mmol}$ ) in THF ( $30\text{cm}^3$ ). A yellow precipitate formed immediately. The supernatant liquid was removed and the solid was washed with petroleum ether ( $3 \times 20\text{cm}^3$ ) and dried in *vacuo* for 3 hours. The yellow solid was  $\text{TiCl}_4 \cdot 2\text{THF}$ .
- (v)  $\text{TiCl}_4$  ( $4.4\text{cm}^3$ ,  $40.12\text{mmol}$ ) was added to a magnetically stirred suspension of  $\text{Na}(\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2)$  ( $6.307\text{g}$ ,  $39.92\text{mmol}$ ) in  $\text{Et}_2\text{O}$  ( $50\text{cm}^3$ ). A yellow precipitate formed immediately but redissolved on stirring. The solution was heated at  $30^\circ\text{C}$  for 2 hours and allowed to cool to room temperature. The volume of solvent was reduced until a black precipitate formed. The black solid proved intractable.

Reaction of the silver salt with  $\text{TiCl}_4$  gave the same result.



### Preparation of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$

$\text{TiCl}_4$  ( $4.5\text{cm}^3$ ,  $41.04\text{mmol}$ ) was added dropwise to a magnetically stirred solution of  $(\text{CH}_3)_3\text{CCO}_2\text{H}$  ( $3.43\text{g}$ ,  $33.63\text{mmol}$ ) in benzene ( $30\text{cm}^3$ ). The resulting red solution was heated at  $60^\circ\text{C}$  for 1 hour and allowed to cool. The volume of solvent was reduced by pumping until yellow solid precipitated. The supernatant liquid was removed, the solid washed with petroleum ether ( $4 \times 30\text{cm}^3$ ) and dried in *vacuo* for 3 hours. (Yield  $7.3\text{g}$ ,  $85\%$ ).

i.r.	1643(m)	1553(m)	1508(s)	1488(s)	1428(s)
	1371(s)	1233(s)	1033(m)	938(w)	778(w)
	613(s)	496(m)	458(m)	403(s)	323(sh) $\text{cm}^{-1}$

$^1\text{H}$  NMR 1.1-1.5 (ms) p.p.m.

$^{13}\text{C}$  NMR 189.6(s), 128.2(s), 26.7 (s) p.p.m.

Analysis for  $\text{TiCl}_3\text{C}_5\text{H}_9\text{O}_2$ :

	Ti	C	H
Calculated:	18.76	23.52	3.55 %
Found:	18.75	23.46	3.66 %

### Preparation of $\text{TiCl}_3(\text{C}_9\text{H}_6\text{NCO}_2)$

$\text{TiCl}_4$  ( $2\text{cm}^3$ ,  $18.24\text{mmol}$ ) was added slowly to a magnetically stirred suspension of  $\text{C}_9\text{H}_6\text{NCO}_2\text{H}$  ( $2.759\text{g}$ ,  $15.9\text{mmol}$ ) in benzene ( $50\text{cm}^3$ ) at  $0^\circ\text{C}$ . A yellow precipitate formed immediately. The suspension was heated at  $80^\circ\text{C}$  for 6 hours, allowed to cool and the solid filtered off. The

solid was washed with petroleum ether (3x10cm<sup>3</sup>) and dried in *vacuo* for 3 hours. (yield 3.74g, 72%).

i.r.	1615(m)	1600(m)	1585(s)	1428(s)	1400(m)
	1370(s)	1315(w)	1275(m)	1230(m)	1175(w)
	1160(m)	1150(m)	1035(m)	970(w)	870(m)
	855(m)	825(m)	790(m)	760(m)	700(s)
	635(w)	610(m)	585(m)	550(w)	530(w)
	495(m)	470(m)	455(m)	415(s)	390(s)
	280(m)	250(m)	cm <sup>-1</sup>		

<sup>1</sup>H NMR 7.37(s) p.p.m.

Analysis for TiCl<sub>3</sub>C<sub>10</sub>H<sub>6</sub>NO<sub>2</sub>

	Ti	C	H	N
Calculated:	14.67	36.8	2.64	2.98 %
Found:	14.7	36.63	1.85	4.29 %

### Preparation of TiCl<sub>3</sub>(o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)

TiCl<sub>4</sub> (6.5cm<sup>3</sup>, 59.27mmol) was added slowly to a magnetically stirred solution of o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H (7.58g, 55.74mmol) in toluene (30cm<sup>3</sup>). An orange precipitate formed immediately. The suspension was heated at 100°C for 2 hours, allowed to cool and the supernatant liquid removed. The yellow solid was washed with petroleum ether (2x30cm<sup>3</sup>) and dried in *vacuo* for 8 hours. (Yield 9.8g, 61%).

i.r.	1600(m)	1580(m)	1550(s)	1505(m)	1430(m)
	1370(w)	1350(s)	1310(m)	1290(m)	1200(m)
	1165(m)	1140(m)	1110(m)	1060(w)	1030(w)
	880(w)	865(w)	835(w)	810(w)	695(w)
	665(m)	620(m)	580(m)	565(m)	540(m)
	490(m)	445(sh)	420(m)	410(m)	380(m)
	270(m)	cm <sup>-1</sup>			

<sup>1</sup>H NMR 6.8-8.3 (b), 2.2-3.0 (b) p.p.m.

Analysis for TiCl<sub>3</sub>C<sub>8</sub>H<sub>7</sub>O<sub>2</sub>

	<sup>Ti</sup>	<sup>C</sup>	<sup>H</sup>	
Calculated:	16.55	33.17	2.42	%
Found:	16.26	32.96	2.39	%

### Preparation of TiCl<sub>3</sub> (p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)

TiCl<sub>4</sub> (2cm<sup>3</sup>, 18.24 mmol) was added dropwise to a magnetically stirred solution of p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H (2.25g, 16.55 mmol) in benzene (30cm<sup>3</sup>). The resulting red solution was heated at 70°C for 2 hours, allowed to cool and the volume of solvent reduced by pumping. On standing at 5 °C a yellow solid precipitated. The supernatant liquid was removed and the solid washed with petroleum ether (2x30cm<sup>3</sup>) and dried in *vacuo* for 4 hours. (Yield 2.75g, 57%).



i.r.	1610(m)	1580(m)	1560(w)	1530(m)	1505(m)
	1410(m)	1350(m)	1320(m)	1185(s)	1160(m)
	1125(m)	1040(w)	1020(m)	860(m)	840(m)
	755(s)	690(w)	645(m)	625(m)	610(m)
	500(m)	460(m)	400(sb)	330(m)	295(m)
	cm <sup>-1</sup>				

<sup>1</sup>H NMR 8.0 (s), 7.39 (s), 2.49(s) p.p.m.

	Ti	C	H
Calculated:	16.55	33.17	2.42 %
Found:	16.40	33.00	2.62 %

**Preparation of TiCl<sub>3</sub>[C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>CO<sub>2</sub>]**

TiCl<sub>4</sub>(1.4cm<sup>3</sup>, 12.77 mmol) was added dropwise to a magnetically stirred solution of C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>CO<sub>2</sub>H (2.05g, 12.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30cm<sup>3</sup>). The resulting red solution was heated at 40°C for 5 hours and allowed to cool. Addition of petroleum ether (BP 100-120°) (60cm<sup>3</sup>) caused an immediate formation of orange precipitate. The supernatant liquid was removed and the solid washed with petroleum ether (3x20cm<sup>3</sup>) and dried in *vacuo* for 2 hours.

i.r.	1610(s)	1595(sh)	1575(m)	1485(m)	1330(m)
	1295(m)	1190(m)	1125(m)	1100(w)	1030(b)
	990(w)	855(m)	795(m)	690(m)	620(b)
	570(m)	525(m)	510(m)	495(m)	440(m)
	405(b)	390(m)	300(b)	cm-1	

<sup>1</sup>H NMR 6.87 (s), 2.26 (s) p.p.m.



Analysis for  $\text{TiCl}_3\text{C}_{10}\text{H}_9\text{O}_2 + 1/3 \text{C}_6\text{H}_{14}$ :

	Ti	C	H
Calculated:	13.09	41.8	4.07 %
Found:	13.45	39.98	4.21 %

Preparation of  $\text{TiCl}_3(\text{CH}_3\text{CH}=\text{CHCO}_2)$

$\text{TiCl}_4$  (6.65cm<sup>3</sup>, 60.64 mmol) was added dropwise to a solution of  $\text{CH}_3\text{CH}=\text{CHCO}_2\text{H}$  (5.145g, 59.83 mmol) in  $\text{CH}_2\text{Cl}_2$  (20cm<sup>3</sup>) at 0°C. The resulting yellow solution was allowed to warm to 20 °C and stirred for 2 hours. The volume of solvent was then reduced by pumping causing the precipitation of yellow solid. The supernatant liquid was removed and the solid washed with hexane (12x20cm<sup>3</sup>) and dried in *vacuo* for 3 hours. (Yield 11.75g, 82%).

i.r.	1635(s)	1580(s)	1425(s)	1300(s)	1270(m)
	1175(s)	1115(m)	1040(m)	1020(m)	960(s)
	920(m)	845(m)	840(m)	690(m)	660(m)
	630(m)	590(m)	535(s)	500(s)	420(s)
	370(s)	325(m)	300(m)	260(m)	230(m)
	cm <sup>-1</sup>				

<sup>1</sup>H NMR 7.75(b) (1H), 6.25(d) (1H), 2.2(d) (3H) p.p.m.

Analysis for  $\text{TiCl}_3\text{C}_4\text{H}_5\text{O}_2$ :

	Ti	C	H
Calculated:	20.00	20.05	2.09 %
Found:	19.90	20.20	2.15 %

### Preparation of $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2)$

$\text{TiCl}_4$  ( $1.7\text{cm}^3$ , 15.5 mmol) was added dropwise to a solution of  $\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{H}$  (2.21g, 14.93 mmol) in  $\text{CH}_2\text{Cl}_2$  ( $20\text{cm}^3$ ) at  $0^\circ\text{C}$ . The resulting orange solution was allowed to warm to  $20^\circ\text{C}$  and stirred for 2 hours. A red solid precipitated and the supernatant liquid was removed then the solid was washed with hexane ( $2 \times 30\text{cm}^3$ ). It was then dried in *vacuo* for 1/2 hour, washed with hexane ( $3 \times 20\text{cm}^3$ ) and dried in *vacuo* for 4 hours. (Yield 2.93g, 65%).

i.r.	1620(s)	1570(m)	1545(s)	1530(sh)	1495(m)
	1290(m)	1265(m)	1240(m)	1200(w)	1180(w)
	1140(m)	1090(w)	1040(m)	1000(w)	980(m)
	865(m)	850(m)	765(s)	675(m)	620(m)
	610(m)	580(m)	550(m)	480(m)	460(m)
	415(s)	350(sh)	260(m)	$\text{cm}^{-1}$	

$^1\text{H}$  NMR 7.7 (s), 7.53 (b), 7.3 (b), 6.65 (b) p.p.m.

Analysis for  $\text{TiCl}_3\text{C}_9\text{H}_7\text{O}_2$ :

	Ti	C	H
Calculated:	15.89	35.83	2.32 %
Found:	15.95	35.74	2.40 %

### Preparation of $\text{TiCl}_4(\text{CH}_3)_3\text{CCOSH}$

$(\text{CH}_3)_3\text{CCOSH}$  ( $3\text{cm}^3$ , 23.64 mmol) was added to a solution of  $\text{TiCl}_4$  ( $4.5\text{cm}^3$ , 41 mmol) in  $\text{CH}_2\text{Cl}_2$  ( $25\text{cm}^3$ ). The resulting red-brown solution was stirred for 1 hour after which dark yellow solid precipitated. The

supernatant liquid was removed and the solid washed with petroleum ether (3x25cm<sup>3</sup>) and dried in *vacuo* for 3 hours. (Yield 3.56g, 49%).

i.r.	2520(m)	1555(sb)	1400(m)	1380(s)	1250(m)
	1225(m)	1045(s)	1025(s)	935(w)	900(s)
	820(m)	770(b)	665(m)	485(m)	460(b)
	400(s)	375(sh)	295(m)	250(m)	cm <sup>-1</sup>

<sup>1</sup>H NMR 0.9 (s) p.p.m.

Analysis for TiCl<sub>4</sub>C<sub>5</sub>H<sub>10</sub>OS:

	Ti	C	H	Cl	S	
Calculated:	15.57	19.49	3.25	46.12	10.39	%
Found:	15.42	19.75	3.48	41.09	9.45	%

### Preparation of Ti[(CH<sub>3</sub>)<sub>2</sub>CHO]<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>)

Ti[(CH<sub>3</sub>)<sub>2</sub>CHO]<sub>4</sub> (5cm<sup>3</sup>, 16.82 mmol) was added to a solution of C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>H (2.05g, 16.81 mmol) in C<sub>6</sub>H<sub>6</sub> (30cm<sup>3</sup>). The resulting colourless solution was heated at 80°C for 8 hours and allowed to cool. The solvent was removed by pumping giving a cream oil. The oil was dissolved in warm hexane (10cm<sup>3</sup>), and when the solution was cooled a white solid precipitated. The supernatant liquid was removed and the solid dried in *vacuo* for 5 hours. (Yield 1.98g, 34%).

i.r.	1720(m)	1620(m)	1600(s)	1560(s)	1540(s)
	1490(m)	1420(s)	1320(m)	1270(m)	1250(sh)
	1135(b)	1065(m)	1000(b)	950(b)	850(s)
	815(sh)	675(m)	620(b)	505(m)	475(b)
	380(m)	360(m)	320(m)	cm <sup>-1</sup>	

<sup>1</sup>H NMR 8.2 (m) (2H), 7.5 (m) (3H), 5.09 (m) (3H), 1.3 (m) (18H) p.p.m.



Analysis for  $\text{TiC}_{16}\text{H}_{26}\text{O}_5$ :

	Ti	C	H
Calculated:	13.85	55.50	7.52 %
Found:	14.21	55.32	7.64 %

Reaction of  $\text{TiCl}_3(\text{RCO}_2)$  ( $\text{R}=\text{C}_6\text{H}_5, (\text{CH}_3)_3\text{C}$  or  $\text{o-CH}_3\text{C}_6\text{H}_4$ ) with THF

e.g.:  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$  (1.67g, 6.06 mmol) was dissolved in THF (20cm<sup>3</sup>) to give a yellow solution. The solution was magnetically stirred for 25 minutes and the solvent removed by pumping until a yellow solid precipitated. The supernatant liquid was removed and the solid washed with hexane (2x20cm<sup>3</sup>) and dried in *vacuo* for 3 hours.

<sup>1</sup>H NMR spectra and elemental analysis showed the yellow solid to be  $\text{TiCl}_4 \cdot 2\text{THF}$ .

Analysis for  $\text{TiCl}_4\text{C}_8\text{H}_{16}\text{O}_2$ :

	Ti	C	H	Cl
Calculated:	18.29	28.75	4.79	42.53 %
Found:	18.51	29.00	4.81	43.48 %

The others were similar.

Reaction of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with THF

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (3.306g, 12.94 mmol) was dissolved in  $\text{C}_6\text{H}_6$  (30cm<sup>3</sup>) to give an orange solution. THF (1.1cm<sup>3</sup>, 13.58 mmol) was added, and the solution immediately turned yellow. After standing for 36 hours yellow crystals formed in the solution. The supernatant liquid was removed and



the crystals washed with petroleum ether (2 x 20 cm<sup>3</sup>) and dried in *vacuo* for 2 hours.

Elemental analyses showed the crystals to be the oxo-compound {TiCl<sub>2</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>]THF}<sub>2</sub>O. The THF used must have contained a trace of water causing hydrolysis of the carboxylate. Comparison of the infra-red and <sup>1</sup>H NMR spectra with those of an authentic sample of {TiCl<sub>2</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>]THF}<sub>2</sub>O confirmed the identification of the crystals.

Analysis for Ti<sub>2</sub>Cl<sub>4</sub>C<sub>18</sub>H<sub>34</sub>O<sub>7</sub>:

	Ti	C	H	
Calculated:	15.97	36.01	5.67	%
found:	16.03	36.01	5.67	%

#### Preparation of {TiCl<sub>2</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>]THF}<sub>2</sub>OH<sub>5</sub>C<sub>6</sub>

TiCl<sub>3</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>] (5.235g, 20.5 mmol) was dissolved in C<sub>6</sub>H<sub>6</sub> (30 cm<sup>3</sup>). THF (1.66 cm<sup>3</sup>, 20.5 mmol) was added to the orange solution which immediately turned yellow. After stirring for 1/2 hour a solution of phenol (1.934g, 20.57 mmol) in C<sub>6</sub>H<sub>6</sub> (5cm<sup>3</sup>) was added. The resulting dark-red solution was stirred for 2 hours, pumped to a red sticky mass and redissolved in toluene (20 cm<sup>3</sup>). On leaving the resulting red solution at -20 °C for 100 hours an orange solid precipitated. The supernatant liquid was removed and the solid was washed with petroleum ether (2 x 10 cm<sup>3</sup>) and dried in *vacuo* for 2 1/2 hours. (Yield 3.88 g, 28%).

i.r.	1750(w)	1650(m)	1605(m)	1585(m)	1540(s)
	1460(m)	1430(s)	1365(m)	1230(s)	1165(m)
	1120(m)	1070(m)	1040(sh)	1020(m)	920(m)
	860(m)	760(s)	690(m)	665(m)	615(m)
	515(m)	460(m)	390(m)	250(m)	cm <sup>-1</sup>

<sup>1</sup>H NMR 7.25(b)(5H), 4.4(m)(8H), 2.07(m)(8H), 1.25(ms)(18H) p.p.m.

Analysis for Ti<sub>2</sub>Cl<sub>4</sub>C<sub>24</sub>H<sub>39</sub>O<sub>7</sub>:

	Ti	C	H	
calculated	14.15	42.55	5.76	%
found:	14.14	42.19	5.71	%

**Reaction of TiCl<sub>3</sub>(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>) with THF and C<sub>6</sub>H<sub>5</sub>OH**

TiCl<sub>3</sub>(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)(1.241g, 4.29 mmol) was dissolved in C<sub>6</sub>H<sub>6</sub> (25cm<sup>3</sup>). THF (0.4 cm<sup>3</sup>, 4.9 mmol) was added to the orange solution which immediately turned yellow. A solution of C<sub>6</sub>H<sub>5</sub>OH (0.202g, 2.15mmol) in C<sub>6</sub>H<sub>6</sub> (5cm<sup>3</sup>) was added. The resulting red solution was heated at 70 °C for 1 hour. On leaving for 36 hours an orange solid precipitated. The supernatant liquid was removed and the solid washed with petroleum ether (3 x 20 cm<sup>3</sup>) and dried in *vacuo* for 3 hours. <sup>1</sup>H and <sup>13</sup>C NMR spectra revealed that no C<sub>6</sub>H<sub>5</sub>O- residues were present so the solid is formulated as [TiCl<sub>2</sub>(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)THF]<sub>2</sub>O.

i.r.	1630 (sh)	1610 (m)	1585 (m)	1510 (s)	1415 (s)
	1310 (m)	1300 (m)	1265 (m)	1215 (w)	1180 (s)
	1155 (m)	1120 (m)	1100 (m)	1045 (m)	1020 (m)
	1010 (m)	960 (w)	925 (m)	860 (m)	855 (m)
	800 (m)	765 (s)	680 (m)	620 (m)	550 (m)
	490 (sh)	460 (s)	400 (s)	385 (s)	355 (s)
	300 (m)	265 (m)	225 (m)	cm <sup>-1</sup>	

<sup>1</sup>H NMR 8.05(b), 7.9 (d), 7.35 (d), 4.75 (m), 2.45 (s), 2.25 (m) p.p.m.

<sup>13</sup>C NMR 176, 146, 131.2, 129.9, 128.45, 75.75, 25.85, 21.8 p.p.m.

Analysis for  $\text{Ti}_2\text{Cl}_4\text{C}_{24}\text{H}_{30}\text{O}_7$ :

	Ti	C	H	Cl
calculated:	14.35	43.13	4.49	21.26 %
found:	12.73	46.42	4.87	18.66 %

Analysis for  $\text{Ti}_2\text{Cl}_4\text{C}_{30}\text{H}_{35}\text{O}_7$ :

	Ti	C	H	Cl
calculated:	12.86	48.33	4.69	19.06 %
found:	12.73	46.42	4.87	18.66 %

Reaction of  $\text{TiCl}_3(\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$  with THF and  $\text{C}_6\text{H}_2\text{Cl}_3\text{OH}$

$\text{TiCl}_3(\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$  (1.405g, 4.85 mmol) was dissolved in  $\text{C}_6\text{H}_6$  (20cm<sup>3</sup>) and a solution of  $\text{C}_6\text{H}_2\text{Cl}_3\text{OH}$  (0.478g, 2.42 mmol) in  $\text{C}_6\text{H}_6$  (10cm<sup>3</sup>) added. The resulting red solution was heated at 65 °C for half an hour and THF (0.4cm<sup>3</sup>, 4.9 mmol) added. The solution was then heated at 70 °C for 16 hours. On allowing the solution to cool orange microcrystals formed. The supernatant liquid was removed and the crystals washed with petroleum ether (3x10cm<sup>3</sup>) and dried in *vacuo* for 6 hours. Elemental analysis and spectral evidence indicated that no  $\text{C}_6\text{H}_2\text{Cl}_3\text{O}$ -residues were present so the product was formulated as  $[\text{TiCl}_2(\text{p-CH}_3\text{C}_6\text{H}_4\text{CO}_2)\text{THF}]_2\text{O}$ .

i.r.	1630(sh)	1610(m)	1585(m)	1510(s)	1415(s)
	1310(m)	1300(m)	1265(m)	1215(w)	1180(s)
	1155(m)	1120(m)	1100(m)	1045(m)	1020(m)
	1010(m)	960(w)	925(m)	860(m)	855(m)
	800(m)	765(s)	680(m)	620(m)	550(m)
	490(sh)	460(s)	400(s)	385(s)	355(s)
	300(m)	265(m)	225(m)	cm-1	



$^1\text{H}$  NMR 8.05(b), 7.9(d), 7.35(d), 4.8(m), 2.45(s), 2.25(m) p.p.m.

Analysis for  $\text{Ti}_2\text{Cl}_4\text{C}_{24}\text{H}_{30}\text{O}_7 + 0.4 \text{ C}_6\text{H}_6$

	Ti	C	H	Cl
calculated:	14.34	45.42	4.64	20.26%
found:	14.53	45.75	4.95	20.66%

### Preparation of $\{\text{TiCl}_2[(\text{CH}_3)_3\text{CCO}_2]\text{EtOAc}\}_2\text{O}_2\text{C}_6\text{H}_4$

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (0.916g, 3.60 mmol) and  $\text{C}_6\text{H}_4(\text{OH})_2$  (0.198g, 1.8 mmol) were mixed and dissolved in EtOAc (30cm<sup>3</sup>). The resulting red solution was stirred for 4 hours and pumped to dryness yielding a red solid. The solid was washed with petroleum ether (6 x 20 cm<sup>3</sup>) and dried in *vacuo* for 3 hours. (Yield ) 0.62g, 47 1/2%).

i.r.	1650 (s)	1580 (m)	1540 (s)	1320 (m)	1280 (w)
	1260 (m)	1230 (m)	1170 (m)	1140 (m)	1100 (sh)
	1065 (w)	1045 (w)	990 (m)	950 (sh)	860 (m)
	780 (m)	690 (w)	610 (m)	550 (w)	515 (w)
	455 (s)	375 (b)	300 (m)	cm <sup>-1</sup>	

$^1\text{H}$  NMR 6.6-7.5(b)(2H), 4.25 (m)(2H), 2.25 (s) (3H), 1.1-1.5 (ms) (12H) p.p.m.

Analysis for  $\text{Ti}_2\text{Cl}_4\text{C}_{24}\text{H}_{38}\text{O}_9$

	Ti	C	H	
calculated:	13.23	39.78	5.25	%
found:	13.33	39.64	5.41	%



## Preparation of $\text{TiCl}_2[(\text{CH}_3)_3\text{CCO}_2](\text{CH}_3\text{COCHCOCH}_3)$

$\text{TiCl}_3[(\text{CH}_3)_3\text{CO}_2]$  (2.813g, 11 mmol) was dissolved in  $\text{C}_6\text{H}_6$  (30  $\text{cm}^3$ ).  $\text{CH}_3\text{COCH}_2\text{COCH}_3$  (1.2  $\text{cm}^3$ , 11.6 mmol) was added to the magnetically stirred solution. The resulting red solution was stirred for 15 hours after which an orange solid precipitated. The supernatant liquid was removed and the solid washed with hexane (2 x 20  $\text{cm}^3$ ) and dried in *vacuo* for 4 hours. (Yield 2.14g, 61%).

i.r.	1830 (w)	1780 (w)	1670 (m)	1530 (s)	1420 (sh)
	1320 (s)	1285 (s)	1230 (m)	1030 (m)	950 (sh)
	935 (m)	800 (m)	670 (m)	600 (m)	540 (m)
	470 (s)	415 (w)	380 (s)	320 (m)	$\text{cm}^{-1}$

$^1\text{H}$  NMR 6.0 (s) (1H), 2.2 (s) (6H), 1.1 - 1.5 (ms) (9H) p.p.m.

Analysis for  $\text{TiCl}_2\text{C}_{10}\text{H}_{16}\text{O}_4$ :

	Ti	C	H	
calculated	15.02	37.63	5.02	%
found:	15.56	37.38	5.34	%

## Reaction of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$ with 2 $\text{CH}_3\text{COCH}_2\text{COCH}_3$

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (0.93g, 3.64 mmol) was dissolved in  $\text{C}_6\text{H}_6$  (12  $\text{cm}^3$ ).  $\text{CH}_3\text{COCH}_2\text{COCH}_3$  (0.8  $\text{cm}^3$ , 7.72 mmol) was added to the magnetically stirred solution. After stirring for  $1/2$  hour an orange solid precipitated. The supernatant liquid was removed and the solid washed with hexane (5 x 15  $\text{cm}^3$ ) and dried in *vacuo* for 3 hours. Comparisons of the infra-red

and  $^1\text{H}$  NMR spectra of the solid with those of  $\text{TiCl}_2(\text{CH}_3\text{COCHCOCH}_3)_2$  show the solid to be  $\text{TiCl}_2(\text{CH}_3\text{COCHCOCH}_3)_2$ .

#### Reaction of $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$ with $\text{CH}_3\text{COCH}_2\text{COCH}_3$

$\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$  (1.665g, 6.05 mmol) was dissolved in  $\text{C}_6\text{H}_6$  (40  $\text{cm}^3$ ) and  $\text{CH}_3\text{COCH}_2\text{COCH}_3$  (0.62  $\text{cm}^3$ , 6mmol) was added to the magnetically stirred solution. The resulting red solution was stirred for 15 hours and pumped to dryness. The red solid was washed with warm hexane (8 x 20  $\text{cm}^3$ ) and dried in *vacuo* for 4 hours. Colourless crystals deposited from the hexane washings; these were identified as  $\text{C}_6\text{H}_5\text{COOH}$  by their infra-red and  $^1\text{H}$  NMR spectra. The red solid was identified as  $\text{TiCl}_2(\text{CH}_3\text{COCHCOCH}_3)_2$  by comparison of its infra-red and  $^1\text{H}$  NMR spectra with those of an authentic sample of  $\text{TiCl}_2(\text{CH}_3\text{COCHCOCH}_3)_2$ . The same result is obtained if the reaction time is reduced to 10 minutes.

#### Reaction of $\text{TiCl}_3(\text{o-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$ with $\text{CH}_3\text{COCH}_2\text{COCH}_3$

$\text{TiCl}_3(\text{o-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$  (2.518 g, 8.7 mmol) was added to magnetically stirred toluene (60  $\text{cm}^3$ ) and  $\text{CH}_3\text{COCH}_2\text{COCH}_3$  (0.9  $\text{cm}^3$ , 8.7 mmol) was added. The suspension dissolved giving a red solution which was stirred for 36 hours. An orange precipitate formed and the supernatant liquid was removed and the solid washed with hexane (2 x 20  $\text{cm}^3$ ). It was then dried in *vacuo* for 5 hours. The infra-red and  $^1\text{H}$  NMR spectra of the orange solid show it to be  $\text{TiCl}_2(\text{CH}_3\text{COCHCOCH}_3)_2$ . This is confirmed by its elemental analysis.

Analysis for  $\text{TiCl}_2\text{C}_{10}\text{H}_{14}\text{O}_4$ :

	Ti	C	H	Cl
calculated:	15.12	37.89	4.45	22.49
found:	15.31	38.08	4.58	22.37



### Reaction of $\text{TiCl}_2(\text{CH}_3\text{COCHCOCH}_3)_2$ with $\text{C}_6\text{H}_5\text{COOH}$

$\text{TiCl}_2(\text{CH}_3\text{COCHCOCH}_3)_2$  (4.578g, 14.45 mmol) was added to a solution of  $\text{C}_6\text{H}_5\text{COOH}$  (1.75g, 14.43 mmol) in  $\text{C}_6\text{H}_6$  (30  $\text{cm}^3$ ). The mixture was heated at 80 °C for 48 hours. A red solid precipitated from the red solution and the supernatant liquid was removed and the solid washed with petroleum ether (4 x 30  $\text{cm}^3$ ). It was then dried in *vacuo* for 3 hours. The infra-red and  $^1\text{H}$  NMR spectra of the solid show it to be unreacted  $\text{TiCl}_2(\text{CH}_3\text{COCHCOCH}_3)_2$ . Benzoic acid was recovered from the supernatant. The same result was obtained when the reactants were heated in  $\text{CH}_2\text{Cl}_2$  for 3 hours.

### Reaction of $\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$ with $\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$

$\text{TiCl}_3(\text{C}_6\text{H}_5\text{CO}_2)$  (0.672 g, 2.44 mmol) and  $\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$  (0.549g, 2.45 mmol) were mixed and dissolved in  $\text{C}_6\text{H}_6$  (30  $\text{cm}^3$ ). The resulting blood red solution was stirred for 16 hours. A red solid precipitated during the stirring. The supernatant liquid was removed and the solid washed with hexane (2 x 20  $\text{cm}^3$ ) and dried in *vacuo* for 3 hours. Comparison of the F.A.B. mass spectrum of the solid with that of an authentic sample of  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)$  shows the red solid to be  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)$ . This is confirmed by its  $^1\text{H}$  NMR spectra and infra-red spectra.

i.r.	1730 (m)	1600 (m)	1585 (m)	1530 (s)	1510 (s)
	1430 (m)	1320 (s)	1290 (s)	1230 (m)	1190 (m)
	1160 (m)	1115 (m)	1070 (m)	1025 (m)	1000 (m)
	935 (m)	840 (w)	820 (m)	790 (w)	770 (m)
	690 (m)	680 (s)	620 (w)	610 (w)	580 (s)
	540 (m)	460 (w)	435 (w)	380 (m)	370 (m)
	350 (s)	300 (m)	250 (m)	$\text{cm}^{-1}$	

$^1\text{H}$  NMR 8.1 (s) (4H), 7.5 (m) (6H), 1.25 (s) (1H) p.p.m.

+ve F.A.B. Mass spectrum of  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)$  (DTR matrix)

m/e 648, 495, 424, 346, 288, 191, 105, 77

+ve F.A.B. Mass spectrum of the red solid (DTR matrix)

m/e 648, 495, 424, 346, 288, 191, 105, 77

### Reaction of $\text{TiCl}_3(\text{o-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$ with $\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$

$\text{TiCl}_3(\text{o-CH}_3\text{C}_6\text{H}_4\text{CO}_2)$  (1.446g, 5mmol) was mixed with  $\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$  (1.136g, 5mmol) and suspended in  $\text{C}_6\text{H}_6$  (60cm<sup>3</sup>). The mixture dissolves forming a red solution. The red solution was stirred for 36 hours. A red solid precipitated. The supernatant liquid was removed and the solid washed with hexane (3 x 30 cm<sup>3</sup>) and dried in *vacuo* for 3 hours. The F.A.B. mass spectrum, infra-red and <sup>1</sup>H NMR spectra of the red solid show it to be  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)$ .

### Reaction of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$ with $\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (3.381g, 15 mmol) and  $\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$  (3.36g, 15 mmol) were mixed and dissolved in  $\text{CH}_2\text{Cl}_2$  (12 cm<sup>3</sup>). The resulting red solution was stirred at 0°C for 1/2 hour. Hexane (60 cm<sup>3</sup>) was added and a red solid precipitated. The supernatant liquid was removed and the solid washed with hexane (3 x 10 cm<sup>3</sup>) and dried in *vacuo* for 3 hours. The F.A.B. mass spectrum, infra-red and <sup>1</sup>H NMR spectra of the red solid reveal that it is  $\text{TiCl}_3(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)$  formed by the displacement of the carboxylate group.



## Reaction of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$ with triphenylphosphine

Triphenylphosphine (4.276g, 16.3 mmol) was added to a magnetically stirred solution of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (4.164g, 16.3 mmol) in  $\text{CH}_2\text{Cl}_2$  (25  $\text{cm}^3$ ). The resulting red solution was stirred for 2 hours and then addition of petroleum ether (50  $\text{cm}^3$ ) caused the precipitation of a brown solid. The supernatant liquid was removed, the solid washed with petroleum ether (2 x 25  $\text{cm}^3$ ) and dried in *vacuo* for 3½ hours. On standing the supernatant liquid turned green.

Recrystallisation of the brown solid from benzene gave blue and orange solids. The  $^1\text{H}$  NMR spectra of all the solids contained resonances at 7.6 p.p.m. due to the phenyl groups of triphenylphosphine. No consistent elemental analysis results were obtained indicating that reduction of the titanium had occurred.

## Reaction of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$ and pyridine

$\text{C}_5\text{H}_5\text{N}$  (1  $\text{cm}^3$ , 12.5 mmol) was added to a magnetically stirred solution of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (3.195g, 12.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (30  $\text{cm}^3$ ). A yellow solid immediately precipitated. The supernatant liquid was removed and the solid washed with petroleum ether (2 x 25  $\text{cm}^3$ ) and dried in *vacuo* for 3 hours.

i.r.	1640 (w)	1610 (s)	1540 (m)	1485 (sh)	1450 (s)
	1330 (w)	1220 (m)	1200 (m)	1165 (m)	1070 (m)
	1050 (m)	1020 (m)	975 (w)	950 (w)	870 (w)
	850 (m)	760 (s)	690 (s)	670 (m)	650 (m)
	645 (m)	615 (m)	465 (m)	440 (s)	350 (s)
	240 (w)	$\text{cm}^{-1}$			

Analysis based on  $\text{TiCl}_3\text{C}_{10}\text{H}_{14}\text{NO}_2$ :

	Ti	C	H	N	Cl
calculated:	14.32	35.88	4.19	4.19	31.85 %
found:	14.04	33.03	3.58	6.35	41.92 %

### Reaction of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$ and pyridine (ii)

$\text{C}_5\text{H}_5\text{N}$  (2.25 cm<sup>3</sup>, 28 mmol) was added to a magnetically stirred solution of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (3.551g, 14 mmol) in  $\text{CH}_2\text{Cl}_2$  (25 cm<sup>3</sup>). A yellow solid immediately precipitated. The supernatant liquid was removed and the solid washed with petroleum ether (3 x 30 cm<sup>3</sup>) and dried in *vacuo* for 3 hours.

i.r.	1610 (s)	1530 (m)	1490 (m)	1450 (s)	1230 (w)
	1220 (m)	1070 (m)	1050 (m)	1020 (m)	760 (m)]
	690 (s)	650 (m)	615 (w)	470 (m)	440 (m)
	370 (s)	290 (m)	240 (w)	cm-1	

Analysis based on  $\text{TiCl}_3\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_4$

	Ti	C	H	N	Cl
calculated :	11.58	49.35	4.6	6.77	25.76 %
found :	11.64	37.03	4.15	6.09	31.77 %

## Hydrolysis Reactions of titanium (IV) monocarboxylates

### Hydrolysis of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$ (Ti:H<sub>2</sub>O ratio 1:2)

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (2.03g, 7.95 mmol) was dissolved in EtOAc (30 cm<sup>3</sup>) which contained H<sub>2</sub>O (0.29 cm<sup>3</sup>, 16 mmol). The resulting pale yellow solution was magnetically stirred for 1½ hours. The volume of solvent was reduced by pumping until a white solid precipitated. The supernatant liquid was removed and the solid washed with petroleum ether (3 x 20 cm<sup>3</sup>) and dried *invacuo* for 3 hours.

(Yield based on  $\text{Ti}_2\text{Cl}_3(\text{EtOAc})_6\text{O}_4$ : 1.23g, 39%).

i.r.	1750 (w)	1680 (s)	1640 (sh)	1540 (sh)	1490 (s)
	1440 (sh)	1315 (m)	1230 (s)	1100 (w)	1040 (m)
	850 (sh)	790 (s)	650 (m)	610 (m)	460 (b)
	380 (b)	cm <sup>-1</sup>			

<sup>1</sup>H NMR 4.45 (m) (2H), 2.5 (s) (3H), 1.35 (t) (3H) p.p.m.

Analysis for  $\text{Ti}_2\text{Cl}_3\text{C}_{24}\text{H}_{48}\text{O}_{16}$ :

	Ti	C	H	Cl
calculated:	12.06	36.26	6.04	13.4 %
found:	11.90	35.17	5.88	13.94%

### Hydrolysis of $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$ (Ti:H<sub>2</sub>O ratio 1:1)

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (1.424g, 5.6mmol) was dissolved in EtOAc (35cm<sup>3</sup>) which contained H<sub>2</sub>O (0.1cm<sup>3</sup>, 5.6mmol). The resulting yellow solution was magnetically stirred for 3 hours. The solution was pumped to dryness giving a cream solid. The solid was recrystallised from  $\text{CH}_2\text{Cl}_2$



(8cm<sup>3</sup>), washed with petroleum ether (2x15cm<sup>3</sup>) and dried in *vacuo* for 3 hours. (Yield based on Ti<sub>2</sub>Cl<sub>4</sub>(EtOAc)<sub>2</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>]<sub>2</sub>O : 0.45g, 25%).

i.r.	1750 (m)	1660 (b)	1510 (sh)	1310 (b)	1240 (b)
	1180 (sh)	1100 (m)	1050 (m)	1020 (sh)	940 (m)
	900 (sh)	850 (b)	610 (b)	470 (b)	360 (b)cm <sup>-1</sup>

<sup>1</sup>H NMR 4.3 (m) (2H), 2.25 (s) (3H), 1.35 (ms) (12H) p.p.m

Analysis based on Ti<sub>2</sub>Cl<sub>4</sub>C<sub>18</sub>H<sub>34</sub>O<sub>9</sub> (impure) :

	Ti	C	H	Cl
calculated:	15.16	34.19	5.38	22.47%
found:	19.83	33.65	5.59	16.27%

### Preparation of {TiCl<sub>2</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>]THF}<sub>2</sub>O

TiCl<sub>2</sub>[(CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>] (3.72g, 14.6 mmol) was dissolved in THF (20cm<sup>3</sup>) which contained H<sub>2</sub>O (0.13cm<sup>3</sup>, 7.3 mmol). The resulting yellow solution was magnetically stirred for 3 hours. On standing yellow crystals deposited from the solution. The supernatant liquid was removed and the crystals washed with petroleum ether (3 x 25 cm<sup>3</sup>) and dried in *vacuo* for 2 hours. (Yield 3.12g, 71%).

i.r.	1660 (m)	1560 (sh)	1530 (s)	1485 (m)	1425 (s)
	1370 (m)	1360 (m)	1350 (m)	1300 (m)	1230 (m)
	1180 (m)	1140 (m)	1040 (m)	1010 (s)	960 (m)
	940 (w)	930 (m)	900 (m)	860 (s)	785 (m)
	680 (s)	615 (m)	600 (m)	550 (m)	460 (s)
	390 (s)	380 (m)	355 (s)	330 (sh)	260 (sh)
	240 (m)	cm <sup>-1</sup>			

<sup>1</sup>H NMR 4.55 (m) (4H), 2.1 (m) (4H), 1.25 (ms) (9H) p.p.m.



Analysis for  $\text{Ti}_2\text{Cl}_4\text{C}_{18}\text{H}_{34}\text{O}_7$ :

	Ti	C	H	
calculated:	15.97	36.01	5.67	%
found:	15.25	36.01	5.67	%

Preparation of  $[\text{TiCl}_2(\text{C}_6\text{H}_5\text{CO}_2) \text{EtOAc}]_2\text{O}$

$\text{TiCl}_2(\text{C}_6\text{H}_5\text{CO}_2)$  (0.453 g, 1.66 mmol) was dissolved in EtOAc (10cm<sup>3</sup>) which contained H<sub>2</sub>O (0.015 cm<sup>3</sup>, 0.83 mmol). The resulting orange solution was heated at 60°C for 40 minutes after which yellow crystals formed. The solution was allowed to cool and the supernatant liquid removed and the crystals washed with petroleum ether (3 x 10 cm<sup>3</sup>). The crystals were dried in *vacuo* for 2 hours. (Yield 0.45 g, 81%).

i.r.	1650 (s)	1600 (m)	1520 (s)	1460 (s)	1410 (s)
	1380 (s)	1320 (s)	1180 (m)	1160 (w)	1150 (w)
	1100 (w)	1070 (w)	1040 (m)	1025 (m)	1010 (w)
	850 (m)	720 (s)	680 (m)	670 (m)	630 (m)
	610 (m)	510 (m)	480 (s)	385 (s)	345 (s)
	320 (m)	260 (w)	cm <sup>-1</sup>		

<sup>1</sup>H NMR 7.3-8.4 (m) (10H), 4.47 (m) (4H), 2.5(s) (6H), 1.35 (t) (6H) p.p.m.

Analysis for  $\text{Ti}_2\text{Cl}_4\text{C}_{22}\text{H}_{26}\text{O}_9$ :

	Ti	C	H	
calculated:	14.26	39.29	3.87	%
found:	14.52	39.16	3.89	%

**Hydrolysis of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  in pyridine (Ti :  $\text{H}_2\text{O}$  ratio 2:1)**

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (1.386 g, 5.43 mmol) was dissolved in pyridine (30  $\text{cm}^3$ ) containing  $\text{H}_2\text{O}$  (0.097  $\text{cm}^3$ , 5.45 mmol). On stirring the yellow solution for 10 minutes a pale yellow precipitate formed. The supernatant liquid was removed and the solid washed with petroleum ether (2 x 30  $\text{cm}^3$ ) and dried in *vacuo* for 4 hours. (Yield based on  $\text{Ti}_2\text{Cl}_5(\text{C}_5\text{H}_5\text{N})_4\text{O}$  : 2.08g, 63%

i.r.	1610 (m)	1560 (s)	1480 (m)	1445 (m)	1430 (m)
	1415 (m)	1220 (m)	1150 (m)	1070 (m)	1040 (m)
	1020 (m)	1000 (w)	970 (w)	940 (w)	780 (s)
	700 (s)	640 (m)	600 (m)	530 (m)	500 (m)
	460 (m)	430 (m)	380 (s)	340 (s)	325 (m)
	290 (m)	240 (m)	$\text{cm}^{-1}$		

$^1\text{H}$  NMR 9.0 (d)(2H), 8.45 (t) (1H), 7.95 (t) (2H) p.p.m.

Analysis based on  $\text{Ti}_2\text{Cl}_5\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}$ :

	Ti	C	H	N	
calculated:	15.83	39.65	3.32	9.25	%
found:	14.17	41.80	5.53	7.78	%

**Hydrolysis of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$ .  $\text{C}_5\text{H}_5\text{N}$  (Ti :  $\text{H}_2\text{O}$  ratio 2:1)**

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  Py (1.818g, 5.44 mmol) was suspended in  $\text{C}_6\text{H}_5\text{Cl}$  (30  $\text{cm}^3$ ) containing  $\text{H}_2\text{O}$  (0.049  $\text{cm}^3$ , 2.72 mmol). The suspension was heated at 130°C for 5 hours. The yellow solid was filtered off and was found to be unreacted starting material. The yellow solution was pumped to dryness producing an orange solid. The orange solid was recrystallised

from  $\text{CH}_2\text{Cl}_2$ , washed with petroleum ether (3 x 20  $\text{cm}^3$ ) and dried in *vacuo* for 4 hours. (Yield based on  $\text{Ti}_2\text{Cl}_4[(\text{CH}_3)_3\text{CCOO}]_2$   $\text{C}_5\text{H}_5\text{NO}$ :0.56g, 38%).

i.r.	1640 (w)	1610 (m)	1540 (s)	1485 (s)	1230 (s)
	1200 (w)	1170 (w)	1125 (w)	1070 (w)	1050 (w)
	1025 (w)	790 (m)	750 (m)	680 (m)	610 (m)
	450 (m)	385 (m)	325 (w)	300 (w)	270 (w) $\text{cm}^{-1}$

$^1\text{H}$  NMR 9.05(d) (2H), 8.6 (t) (1H), 8.1 (t) (2H), 1.25 (ms) (18H) p.p.m.

## TITANIUM-MAGNESIUM COMPLEXES

### Reaction of $\text{Mg}(\text{CH}_3\text{CO}_2)_2$ and $\text{TiCl}_4$

$\text{TiCl}_4$  (3.8  $\text{cm}^3$ , 34.8 mmol) was added slowly to a magnetically stirred suspension of anhydrous  $\text{Mg}(\text{CH}_3\text{CO}_2)_2$  (4.948g, 34.8 mmol) in  $\text{CHCl}_3$  (30  $\text{cm}^3$ ). The resulting yellow suspension was heated at  $50^\circ\text{C}$  for 4 hours. The cream solid was filtered off, washed with petroleum ether (3 x 20  $\text{cm}^3$ ) and dried in *vacuo* for 3 hours. Magnesium analysis of the solid shows it to be unreacted  $\text{Mg}(\text{CH}_3\text{CO}_2)_2$

Analysis for  $\text{MgC}_4\text{H}_6\text{O}_4$ :

	Mg
calculated:	17.08%
found:	17.52%



**Preparation of  $\text{TiMgCl}_4(\text{C}_6\text{H}_5\text{CO}_2)_2(\text{CH}_3\text{COOC}_2\text{H}_5)_2$**

$\text{TiCl}_4$  (1.2cm<sup>3</sup>, 10.9 mmol) was added dropwise to a magnetically stirred solution of  $\text{Mg}(\text{CH}_3\text{CO}_2)_2$  (1.55g, 10.9 mmol) in EtOAc (30cm<sup>3</sup>). The resulting yellow solution was heated at 77 °C for 10 hours. The solution was then pumped to dryness giving a yellow solid. The solid was recrystallised from  $\text{CH}_2\text{Cl}_2$  (10 cm<sup>3</sup>) and dried in *vacuo* for 3 hours. (Yield 3.21g, 47%).

i.r.	1690 (sh)	1640 (s)	1600 (m)	1520 (m)	1300 (m)
	1170 (m)	1090 (w)	1070 (w)	1040 (m)	845 (m)
	770 (w)	665 (m)	600 (m)	470 (b)	370 (b)
	270 (sh)	cm-1			

<sup>1</sup>H NMR 7.3 - 8.5 (m) (5H), 4.35 (m) (2H), 2.35 (s) (3H), 1.35 (t) (3H) p.p.m.

Analysis for  $\text{TiMgCl}_4\text{C}_{22}\text{H}_{26}\text{O}_8$ :

	Ti	Mg	C	H	Cl
calculated:	7.58	3.85	41.76	4.11	22.46 %
found:	8.07	2.55	41.33	4.56	22.01 %

**Reaction of  $\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  with  $\text{MgO}$**

$\text{TiCl}_3[(\text{CH}_3)_3\text{CCO}_2]$  (2.722 g, 10.66 mmol) was added to a magnetically stirred suspension of  $\text{MgO}$  (0.43g, 10.66 mmol) in EtOAc (45cm<sup>3</sup>). The yellow suspension was heated at 77 °C for 8 hours. The resulting yellow solution was pumped to dryness giving a yellow solid. The solid was washed with hexane (3 x 30 cm<sup>3</sup>) and dried in *vacuo* for 4 hours.



i.r.	1755 (m)	1700 (b)	1650 (b)	1520 (sh)	1425 (sh)
	1320 (m)	1240 (m)	1170 (w)	1120 (w)	1050 (m)
	860 (w)	790 (w)	620 (m)	480 (b)	350 (w)
	310 (w)	cm-1			

$^1\text{H}$  NMR 4.3 (m) (2H), 2.2 (s) (3H), 1.05 - 1.5 (m) (12H) p.p.m.

Analysis for  $\text{TiCl}_3\text{C}_9\text{H}_{17}\text{O}_4$ . MgO mixture:

	Ti	C	H	Mg
calculated:	12.49	28.17	4.46	6.33%
found:	12.11	30.33	5.34	5.43%

### Preparation of a standard $\text{MgCl}_2$ solution

A standard solution of anhydrous  $\text{MgCl}_2$  in EtOAc (0.5M) was prepared by adding EtOAc (500  $\text{cm}^3$ ) to solid anhydrous  $\text{MgCl}_2$  (24g, 0.25M) and refluxing for 18 hours. All the solid dissolves but on standing white crystalline deposits formed. The deposits are the ethyl acetate adduct of  $\text{MgCl}_2$ .

### Reaction of the $\text{MgCl}_2$ standard solutions with $\text{TiCl}_4$ , THF and $p\text{-CH}_3\text{C}_6\text{H}_4\text{COOH}$

$\text{TiCl}_4$  (5.5  $\text{cm}^3$ , 50 mmol) was added slowly to a standard solution of  $\text{MgCl}_2$  in EtOAc (50 $\text{cm}^3$ , 25 mmol). The resulting yellow solution was heated at 70 °C for 4 hours. The solution was allowed to cool and  $p\text{-CH}_3\text{C}_6\text{H}_4\text{COOH}$  (6.8g, 50 mmol) was added. The red solution was stirred and heated at 70 °C for 2 hours. The volume of solvent was reduced by

pumping and THF (20 cm<sup>3</sup>) was added. This caused the immediate precipitation of yellow solid. The supernatant liquid was removed and the solid washed with petroleum ether and dried in *vacuo* for 3 hours. The solid can be recrystallised from CH<sub>2</sub>Cl<sub>2</sub> to give small yellow crystals. A magnesium analysis of the solid shows it contains no magnesium at all.

### Preparation of TiMgCl<sub>6</sub>(C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>)(EtOAc)<sub>2</sub>

A MgCl<sub>2</sub> standard solution in EtOAc (21.5 cm<sup>3</sup>, 10.75 mmol) was added to a magnetically stirred solution of TiCl<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>) (2.96g, 10.75 mmol) in EtOAc (20 cm<sup>3</sup>). The resulting yellow solution was heated at 55 °C for 4 hours. The solution was then filtered and pumped to dryness giving a yellow solid. The solid was washed with petroleum ether (4 x 20 cm<sup>3</sup>) and dried in *vacuo* for 3 hours. If the solid is heated it turns a greenish-yellow colour. (Yield 3.9g, 62%).

i.r.	1680 (m)	1600 (m)	1570 (m)	1490 (m)	1400 (sh)
	1305 (s)	1180 (m)	1150 (m)	1100 (w)	1070 (w)
	1040 (m)	1025 (m)	1010 (w)	940 (w)	850 (s)
	820 (w)	770 (sh)	685 (w)	670 (m)	600 (s)
	490 (s)	375 (b)	cm <sup>-1</sup>		

<sup>1</sup>H NMR 7.55 - 8.2 (m) (5H), 4.4 (m) (4H), 2.35 (s) (6H), 1.35 (t) (6H) p.p.m.

Analysis for TiMgCl<sub>5</sub>C<sub>15</sub>H<sub>21</sub>O<sub>6</sub>:

	Ti	Mg	
calculated:	8.74	4.43	%
found:	8.53	4.22	%

## Preparation of $\text{TiMgCl}_6(\text{HOC}_6\text{H}_4\text{CO}_2\text{H})(\text{EtOAc})_2$

A standard solution of  $\text{MgCl}_2$  in EtOAc ( $11.5 \text{ cm}^3$ , 5.75 mmol) was added to a magnetically stirred solution of  $\text{TiCl}_4$  ( $0.65 \text{ cm}^3$ , 5.9 mmol) in EtOAc ( $30 \text{ cm}^3$ ). The yellow solution was heated at  $70^\circ\text{C}$  for 5 hours, allowed to cool and filtered. *p*- $\text{HOC}_6\text{H}_4\text{COOH}$  (0.8g, 5.8 mmol) was added to the stirred solution giving an immediate orange precipitate. The supernatant liquid was removed and the solid washed with hexane ( $3 \times 20 \text{ cm}^3$ ) and dried in *vacuo* for 4 hours. (Yield 2.31g, 67%).

i.r.	3390 (b)	1680 (s)	1605 (sh)	1595 (s)	1490 (sh)
	1415 (sh)	1260 (b)	1160 (m)	1100 (w)	1040 (m)
	1010 (w)	900 (m)	860 (m)	770 (m)	680 (b)
	615 (m)	545 (w)	470 (m)	410 (m)	350 (sh)
	280 (w)	cm-1			

### Analysis for $\text{TiMgCl}_6\text{C}_{15}\text{H}_{22}\text{O}_7$ :

	Ti	Mg	
calculated:	8.01	4.06	%
found:	8.28	3.636	%

## X-ray Crystallography

Single crystals suitable for X-ray structure determinations were obtained by the liquid diffusion method. A small amount of compound is dissolved in an appropriate solvent in a small tube and hexane layered carefully onto the solution. As the hexane diffuses into the solution crystals form at the interface. The crystals are then mounted under argon in 0.5 mm or 0.3 mm Lindemann tubes.



Data was collected with a Syntex P21 four circle diffractometer and the structures solved using SHELXTL<sup>(181)</sup> on a Data General DG 30 computer system.

## Molecular Weights

Molecular weights were determined using the freezing point depression method. A weighed sample of compound was dissolved in benzene (10 cm<sup>3</sup>) and the solution introduced into the N<sub>2</sub> filled freezing point measurement device. (Figure 6.1). The solution was then frozen by an ice/water bath while being stirred. The freezing point of the solution was noted and compared to that of pure benzene to determine the freezing point depression. The molecular weight was then calculated using the formula:

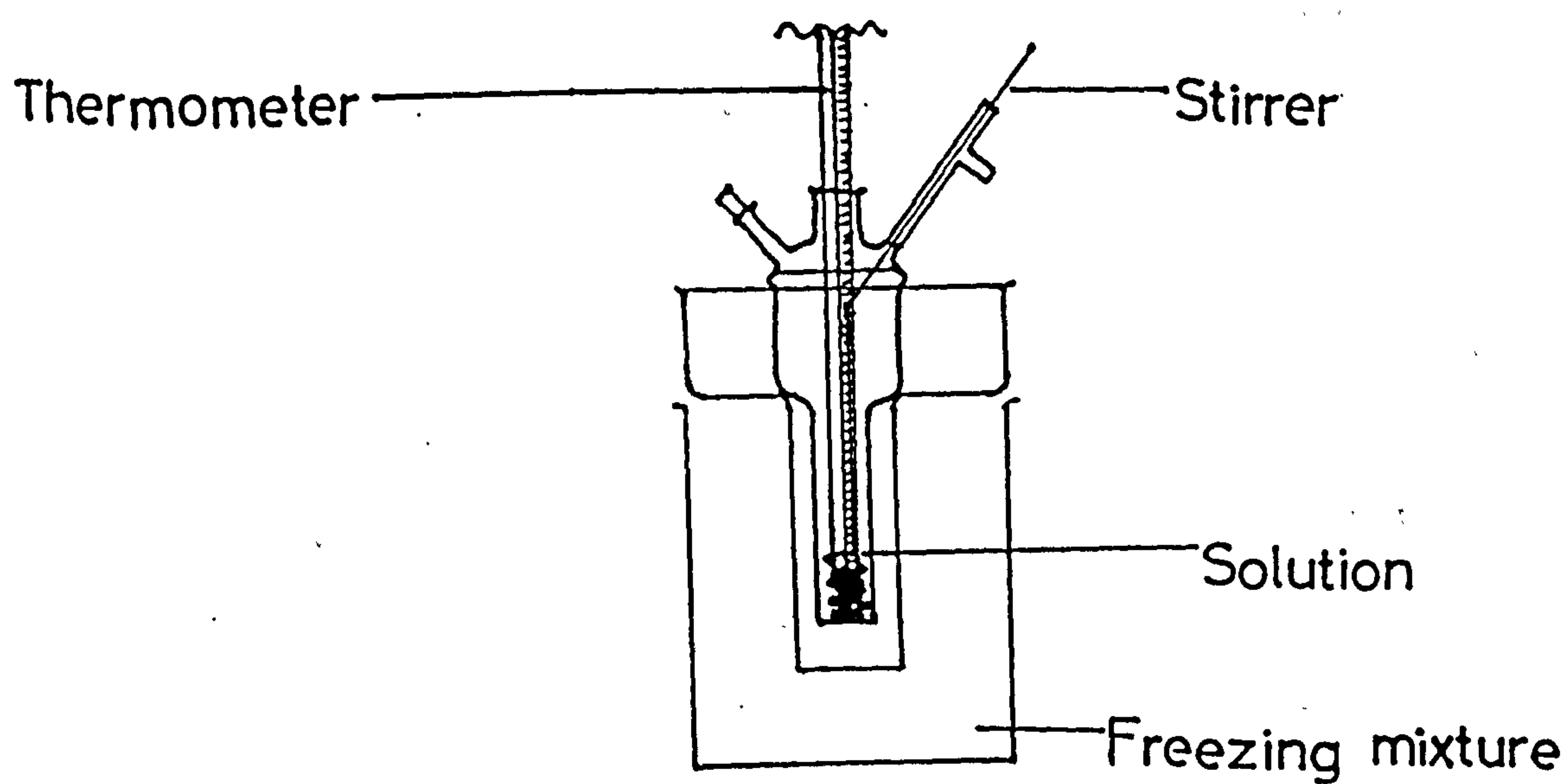
$$M_B = FW_B / \Delta T$$

$M_B$  = Molecular Weight,  $F$  = freezing point depression constant for C<sub>6</sub>H<sub>6</sub>,

$W_B$  = mass of compound used and  $\Delta T$  = freezing point depression.



Figure 6.1 Freezing Point Measurement Device

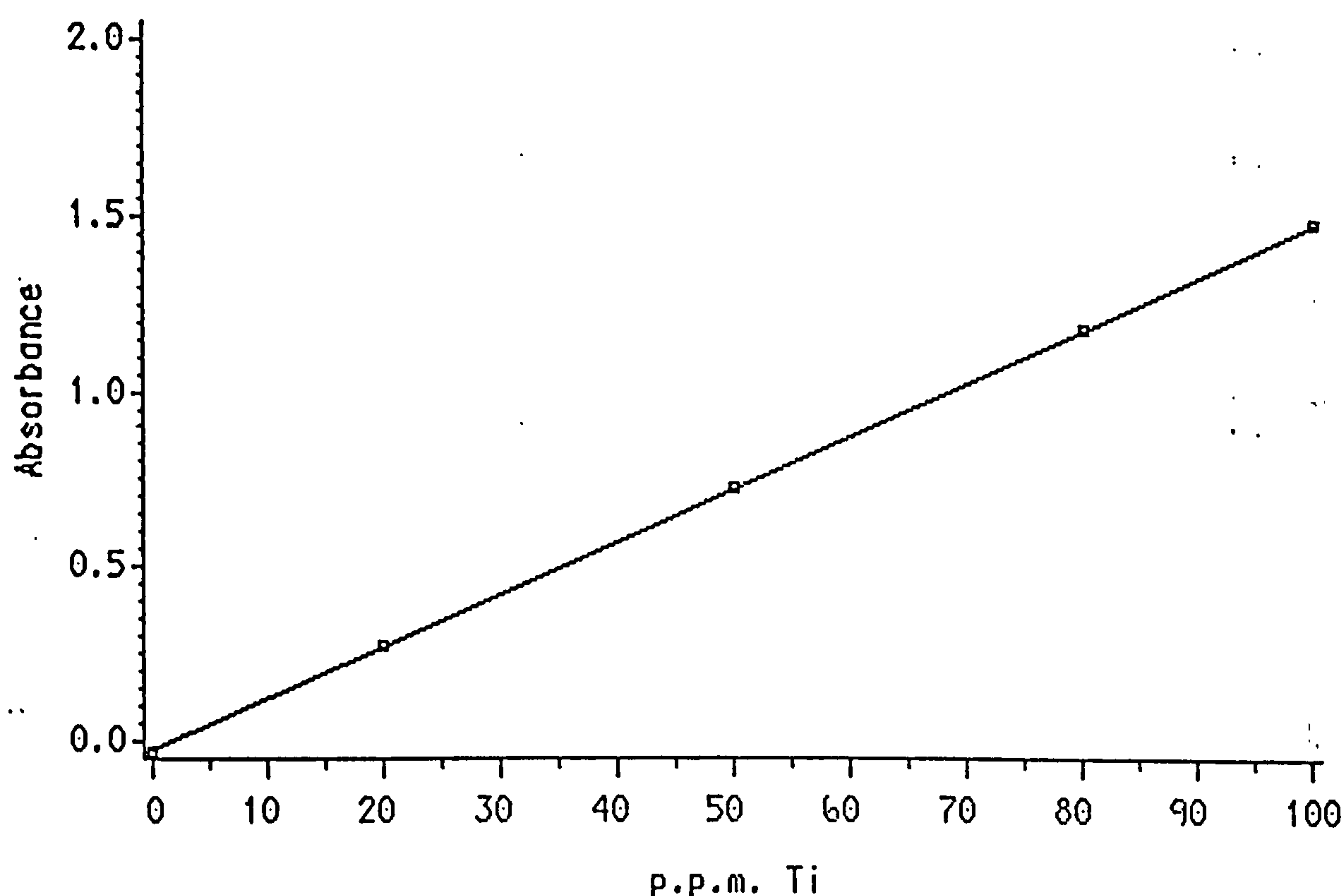


## Analytical Techniques

Titanium was determined by using the absorbance of titanium (IV) peroxo-species at 410 nm in acid solution. At titanium concentrations between 10-100 p.p.m. the yellow or orange solutions obey the Beer-Lambert Laws.

A small amount of the test sample (0.01-0.1 g) was hydrolysed using concentrated  $\text{H}_2\text{SO}_4$ . The volume of the solution was made up to 99  $\text{cm}^3$  using an approximately 50/50 mixture of 2M  $\text{H}_2\text{SO}_4$  and distilled water. Then 1  $\text{cm}^3$  of 20 volume  $\text{H}_2\text{O}_2$  was added. The absorbance of the resulting yellow solution was measured with a Pye-Unicam SP6-250 Spectrophotometer in a 1 cm polycarbonate cuvette and compared with standards, using the graph shown in figure 6.2.

Figure 6.2: Titanium Analysis Graph



Magnesium was determined by atomic absorption spectrophotometry, using a Varian AA6 instrument. Magnesium was detected in the concentration range  $0.5 \mu\text{g/ml}$  -  $2.0 \mu\text{g/ml}$  at a wavelength of  $285.4\text{nm}$  using a  $\text{N}_2\text{O}/\text{C}_2\text{H}_2$  flame.

The test samples were prepared by dissolving an appropriate amount of compound in concentrated  $\text{H}_2\text{SO}_4$  adding  $5 \text{ cm}^3$  of a standard solution of  $\text{KHSO}_4$  ( $80\text{g KHSO}_4$ ,  $40 \text{ cm}^3 \text{ H}_2\text{SO}_4$ ,  $400 \text{ cm}^3 \text{ H}_2\text{O}$ ) and making the volume up to  $100 \text{ cm}^3$  with distilled water. The instrument was calibrated using solutions made up from commercially available standard solutions (B.D.H. Ltd.).

Some chloride analysis was performed using the Volhard method. The sample ( $\sim 0.1\text{g}$ ) was hydrolysed with dilute  $\text{HNO}_3$  and made up to  $100$

cm<sup>3</sup>. Excess AgNO<sub>3</sub> solution was added to aliquots of the sample solution and the resulting precipitate of AgCl coagulated with nitrobenzene. The unreacted AgNO<sub>3</sub> was then titrated against standard KSCN solution with a drop of [NH<sub>4</sub>][Fe(SO<sub>4</sub>)<sub>2</sub>] as indicator. The solution becomes red at the end point as [Fe(SCN)<sub>6</sub>]<sup>3-</sup> is formed.

Carbon, hydrogen and nitrogen were determined commercially by either Elemental Micro-Analysis Ltd., Beaworthy, Devon or Butterworth Laboratories Ltd., Teddington, Middlesex. Sulphur was determined commercially by Butterworth Laboratories Ltd., Teddington, Middlesex.

## Instrumentation

Routine <sup>1</sup>H NMR spectra were recorded using a Perkin Elmer R34 spectrometer. High resolution and variable temperature <sup>1</sup>H NMR spectra (400 MHz) were recorded using a Bruker WH400 spectrometer as were <sup>13</sup>C (100 MHz) and <sup>17</sup>O (54.2 MHz) NMR spectra.

If the NMR sample was insoluble in CDCl<sub>3</sub> then CD<sub>2</sub>Cl<sub>2</sub> or C<sub>6</sub>D<sub>6</sub> were used as solvents. Deuterated toluene was used for variable temperature work. Infra-red spectra were recorded in the range 4000-200 cm<sup>-1</sup> using a Perkin-Elmer 580B spectrophotometer with samples as mulls in nujol between CsI plates, unless otherwise stated.

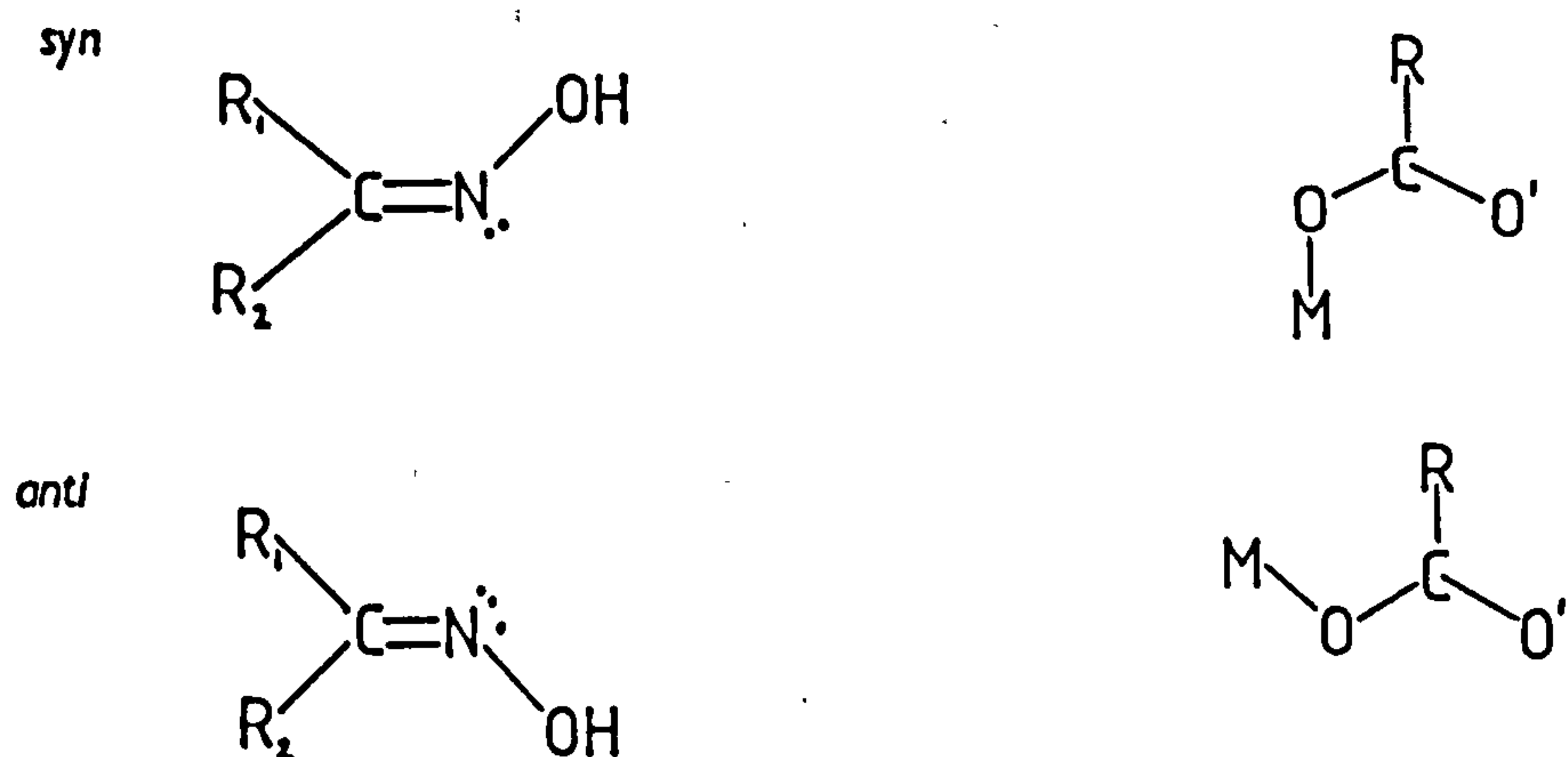


## **APPENDIX 1.**

## Appendix 1

### The Nomenclature of Bidentate Bridging Carboxylates

The present system of naming bidentate bridging carboxylates was proposed in 1959 by Martin and Waterman<sup>(57)</sup> The nomenclature was an extension of that used at the time in organic chemistry to describe oximes and diazoates. The *syn* and *anti* forms of an oxime are illustrated below along with the corresponding carboxylate species.



In these cases the positions of R, and OH are examined relative to the C=N bond, if they are *cis* the oxime is *syn*, if *trans* the oxime is *anti*. Similarly the positions of the metal and O' are examined relative to the C-O single bond in the carboxylate. Repeating the process for the other metal atom and O relative to the C-O' single bond gives the familiar *syn-syn*, *anti-syn*, *anti-anti* nomenclature.

However current organic nomenclature does not use *syn* and *anti* but the prefixes Z and E. (Z from German *zusammen* = together, E from German *entgegen* = opposite). The groups to be compared are placed in order using the Sequence Rules. Table (A1.1).

If the two ligands of highest precedence are on the same side of the C=N axis the compound is Z, if on opposite sides the compound is E.

In the case of the metal carboxylates the two ligands of highest precedence are the metal and O'. These are compared relative to the C-O axis.

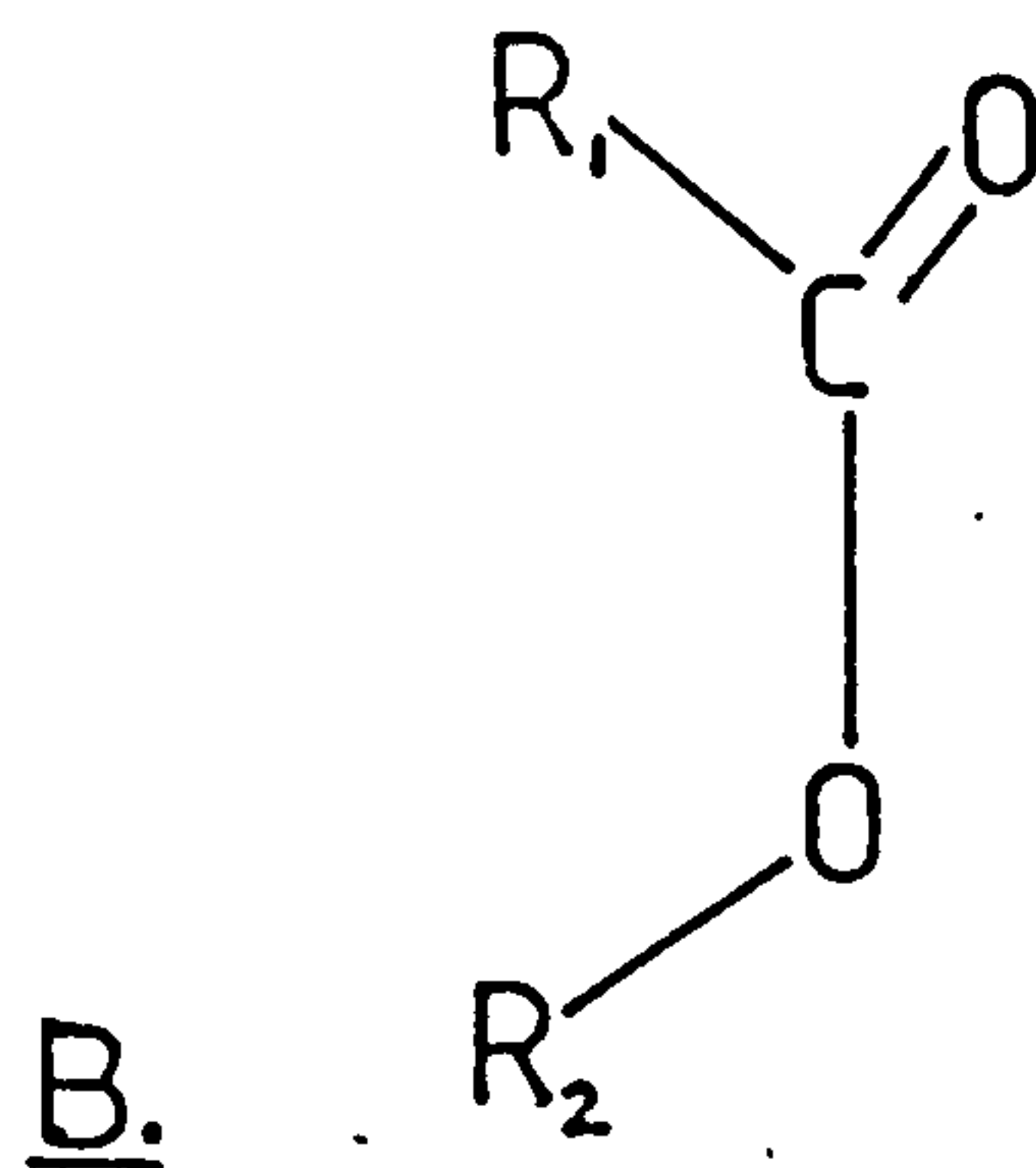
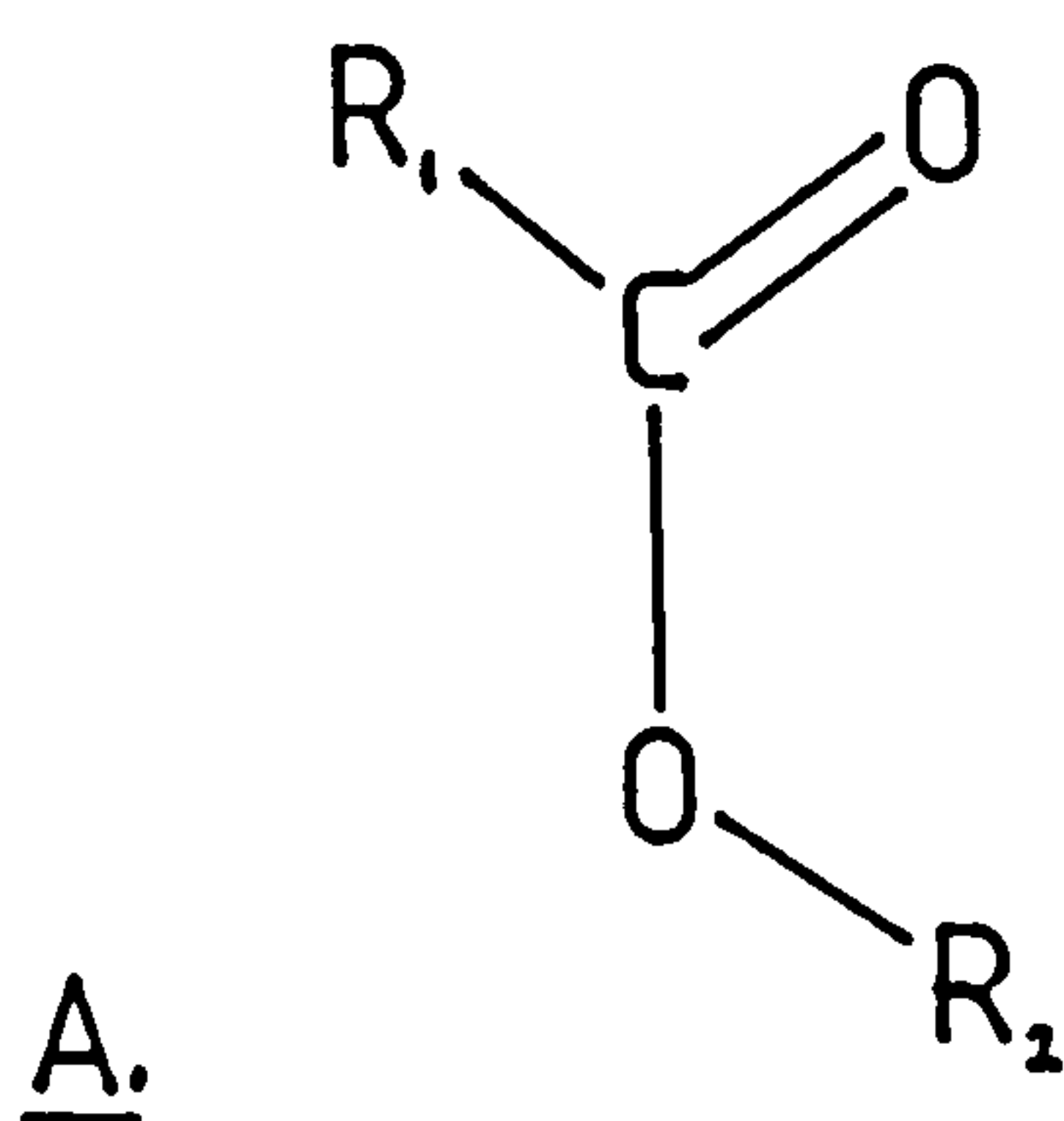
So the *syn-syn* mode becomes Z,Z, the *anti-syn* mode becomes E,Z and the *anti-anti* mode becomes E,E.

Unfortunately if the first atom in the alkyl chain R has an atomic number greater than eight then the *syn-syn* mode becomes E,E, the *anti-syn* mode Z,E and the *anti-anti* mode Z,Z.

This could become confusing so an alternative nomenclature system is presented here:

### Ester Type Nomenclature.

It is proposed that the current organic nomenclature for carboxylate esters be used to describe bidentate bridging carboxylates. The esters exist as two rotamers (A and B below) differing only due to rotation around the C-O single bond.



Rotamer A is the *s-cis* or syncoplanar form. Rotamer B is the *s-trans* or antiperiplanar form. In the syncoplanar form R<sub>2</sub> and =O are on the same side of the C-O axis. In the antiperiplanar form R<sub>2</sub> and =O are on opposite sides of the C-O axis.

In the carboxylate case R<sub>2</sub> is a metal and =O becomes the other carbon-oxygen single bond. Therefore the *syn-syn* mode becomes syncoplanar-syncoplanar, the *anti-syn* mode becomes antiperiplanar-syncoplanar and the *anti-anti mode* becomes antiperiplanar-antiperiplanar.

This nomenclature has several advantages:

- (i) It correctly identifies the carboxylate as being a planar species avoiding confusion with the *syn/anti* nomenclature used in ethane derivatives.
- (ii) It may be used to name unidentate carboxylates giving precise information about the orientation of the C=O group.
- (iii) The nomenclature may be conveniently abbreviated, syncoplanar-syncoplanar to *syn-syn*, antiperiplanar-syncoplanar to *anti-syn* and antiperiplanar-antiperiplanar to *anti-anti*. This allows easy translation from the present nomenclature.



**Table A1.1 : The Sequence Rules.**

- (i) Ligands are arranged in order of decreasing atomic number  
e.g.  $\text{Cl} > \text{O} > \text{C} > \text{Li}$  etc.
- (ii) Isotopes are arranged in order of decreasing mass number  
e.g.  $^{37}\text{Cl} > ^{35}\text{Cl}$ .
- (iii) A lone pair of electrons is placed below H in the precedence order.
- (iv) Double or triple bonds are treated by assuming that each bonded atom is duplicated or triplicated.
- (v) If comparison of the atoms bonded to the centre of interest does not yield a precedence then the atoms bonded to one of the equivalent atoms are considered.

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## *Guidelines*

The guidelines used when preparing this thesis were:

University of Warwick Department of Chemistry, *Guidelines to assist candidates in matters related to their work for a higher degree by research and in the preparation of their theses*, October 1986.